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RESEARCH PAPER RP1531

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CLASSIFICATION OF CARBOHYDRASES

By William Ward Pigman

ABSTRACT

A system for the classification of the carbohydrases has been proposed by Weidenhagen, and, although it has considerable value, it also has a number of obvious deficiencies. It is demonstrated in the present paper that many of these difficulties may be obviated by considering the individual enzymes of Weidenhagen, e. g., α-glucosidase, as classes of enzymes of similar action but varying according to the source. The results of more recent studies of the specificity of the carbohydrases are considered, and the action of enzymes on pentoses, hexoses, and heptoses of similar ring conformations is interpreted. These results and the conception of the complex nature of Weidenhagen's individual enzymes are utilized in the establishment of a provisional system for the classification of the carbohydrases.

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I. INTRODUCTION

Certain enzymes, found in many products of biological origin, catalyze the hydrolysis and synthesis of glycosides, oligosaccharides, and polysaccharides. As a group, they are usually termed "carbohydrases" or "glycosidases." In the present discussion, the entire group will be designated "carbohydrases," those hydrolyzing glycosides and oligosaccharides as "glycosidases," and those hydrolyzing polysaccharides as "polysaccharidases." A system for the classification of these enzymes, presented by Weidenhagen, has proved of considerable value and has stimulated much research, but it has received a great deal of criticism. The purpose of the present paper is to show that by making a few changes in the Weidenhagen postulates, a system of considerably more general validity may be developed. In addition, the results of more recent researches will be considered and incorporated into a system for the classification of the carbohydrases. Although the modified system does not entirely possess the appealing simplicity of the original Weidenhagen classification, it agrees much better with the experimental results. In any case, it is believed that the function of a system of classification is

principally to illustrate the connection between the structures of the substrates and the action of the enzymes and not, as stated by Hofmann,[1] merely to reduce the number of enzymes to a few individuals. Additional experimental work is required before the new system can be substantiated, and it is hoped that workers in the field will test the more questionable points as the opportunities arise.

In its original form, the Weidenhagen system[2] demanded that there be only one enzyme for each glycosidic type. One enzyme should hydrolyze all β-*D*-glucosides (β-glucosidase), one all α-*D*-glucosides (α-glucosidase), one all α-*D*-galactosides (α-galactosidase), etc. The disaccharides were considered as glycosides, and the same enzyme was made responsible for the hydrolysis of related polysaccharides, disaccharides, and glycosides. The system required that β-glucosidase hydrolyze alkyl and aryl β-*D*-glucosides, cellobiose, gentiobiose, and cellulose. Similarly, α-glucosidase should catalyze the hydrolysis of alkyl and aryl α-*D*-glucosides as well as maltose, and invertase (β-fructofuranosidase) should hydrolyze both sucrose and inulin. Obvious disagreement with the experimental facts later led to the somewhat modified theory, in which the enzymes hydrolyzing polysaccharides (polysaccharidases) were separated, at least provisionally, from the enzymes hydrolyzing the glycosides and oligosaccharides (glycosidases).[3]

II. CLASSIFICATION OF CARBOHYDRASES

The principal differences between the system proposed in the present paper and that of Weidenhagen are (1) the individual enzymes of his system are now considered as classes of enzymes acting on the same substrates but with different specificities and other properties and (2) the more recent knowledge of the action of carbohydrases on pentoses, hexoses, and heptoses of similar structures and configurations is introduced into the system of classification. The modified classification is summarized in table 1, which gives the main enzyme classes now known and the substrates on which they act.

TABLE 1.—*Detailed classification of carbohydrases*

Enzyme class	Other or older names for members of class	Substrates [a]
GLYCOSIDASES HYDROLYZING SIMPLE GLYCOSIDES AND OLIGOSACCHARIDES [b]		
β-Glucosidases	Emulsin, cellobiases, gentiobiases.	β-*D*-Glucosides, β-*D*-xylosides, cellobiose, gentiobiose, β-*D*-and *L-glycero-D-gluco*-aldoheptosides (?), β-*D*-glucuronides (?).
α-Glucosidases	Maltases, trehalases	α-*D*-Glucosides, α-*D*-xylosides (?) maltose, sucrose, α-*D*- and *L-glycero-D-gluco*-aldoheptosides (?).
β-Galactosidases	Lactases	β-*D*-Galactosides, α-*L*-arabinosides, β-*D*-fucosides (?), lactose, β-*D*- and *L-glycero-D-galacto*-aldoheptosides, α-*D*-galacturonides (?).
α-Galactosidases	Melibiases	β-*D*-Galactosides, β-*L*-arabinosides, α-*D*-fucosides (?), melibiose, α-*D*- and *L-glycero-D-galacto*-aldoheptosides.
β-Fructofuranosidases or invertases.	Sucrase	Fructofuranosides; sucrose; inulin (?).
α-*D*-Mannosidases		α-*D*-Mannosides, α-*D*-lyxosides, β-*D*- and *L-glycero-D-manno*-aldoheptosides (?).
β-Thioglucosidases	Myrosin	β-Thioglucosides, thioxylosides (?), etc.
Nucleosidases		*N*-Glycosides, nucleosides.

Footnotes are at end of table.

[1] E. Hofmann, Biochem. Z. **285**, 429 (1936).
[2] R. Weidenhagen, Ergeb. Enzymforsch. **1**, 168 (1932).
[3] R. Weidenhagen, in Handbuch der Enzymologie by Nord-Weidenhagen, p. 519 (Akademische Verlagsgesellschaft, Leipzig, 1940).

TABLE 1.—*Detailed classification of carbohydrases*—Continued

Enzyme class	Other or older names for members of class	Substrates [a]
	POLYSACCHARIDASES [b]	
Amylases	Diastases	Starch, glycogen.
α-Amylases	Dextrogenic or liquifying amylases.	Branched chain starch and glycogen.
Bacillus macerans amylase	Dextrogenic or liquifying amylases.	Glycogen and branched chain starch.
Disaggregating amylases	Amylophosphatase	Whole starches are broken, possibly at phosphate linkages, into large molecules.
β-Amylases	Saccharifying amylase	Straight chain starches (poly-α-*D*-glucosides).
Phosphoamylases	Phosphorylases	Straight chain starches and glycogen by process involving phosphorylation.
Inulases (possibly identical with invertases).		Inulin, irisin and poly-fructofuranosides.
Cellulases		Cellulose and poly-β-glucopyranosides, certain glucosans.
Hexosanases and pentosanases.	Cytases	Hexosans, pentosans and hemicelluloses.
Chitinases		Chitin and lower molecular weight homologs.
Pectinases		Pectins.
Protopectinase		Hydrolyzes native pectins *in situ* to soluble pectins.
Pectolase		Polygalacturonides.
(Pectase)		An esterase hydrolyzing esters of galacturonic acid.

[a] The nomenclature adopted for the heptoses follows that suggested by the Committee on Carbohydrate Nomenclature of the American Chemical Society. The "*D-glycero*" refers to the configuration of the terminal asymmetric carbon and the "*D-gluco-*" or "*D-galacto*" to the configuration of carbons 2, 3, 4, and 5. The alpha-beta nomenclature of Isbell is followed except for the arabinosides, which are named by Hudson's system.

As far as known, the glycosides followed by question marks have never been tested, at least under sufficiently drastic conditions to indicate "nonhydrolyzability." The others have been tested for at least one member of the enzyme class, usually the corresponding enzyme in almond emulsin.

[b] There is probably overlapping between the two main classes of carbohydrases, but, in general, the action of the one group of enzymes on the substrates of the second class is small and may usually be neglected.

III. POSTULATES AND EVIDENCE FOR THE SYSTEM OF CLASSIFICATION

1. GLYCOSIDASES

The classification presented depends on the validity of the following assumptions, some adequately and some inadequately established.

1. Changes in the aglycon group affect the rate of enzymic hydrolysis of the glycoside, but profound changes are required before the rate becomes inappreciable (aglycon specificity).

2. Glycosides having different configurations for the glycosidic carbon, require different enzymes (alpha-beta specificity).

3. Enzymes from different sources which catalyze the same reaction vary in the specificity which they exhibit, i. e., they are affected to different extents by changes in the aglycon and sugar groups.

4. Substitution of the ring hydroxyls of hydrolyzable glycosides by other groups makes the glycosides unhydrolyzable by the same enzyme.

5. Changing the configuration of one or more ring carbons or of the ring type, e. g., from pyranose to furanose, makes a hydrolyzable glycoside unhydrolyzable by the same enzyme. This brings together the previous "ring", "*D, L*", and "sugar" specificity (ring-type specificity).

6. Changes made outside of the sugar ring affect the rate of enzymic hyrolysis, but usually do not result in requiring a new enyzme for the hydrolysis.

7. In natural products, only those enzymes are to be expected which are capable of hydrolyzing glycosides of the same basic ring type as that of a naturally occuring glycoside.

8. *Thio-* and *N*-glycosides, with the glycosidic linkage taking place through a sulfur or nitrogen atom rather than an oxygen atom, require enzymes different from those hydrolyzing the ordinary glycosides.

Some of these assumptions are corollaries of others. Thus, 2 is a special case of 5 and 1 of 6, but their importance makes it desirable to list them separately. The status of the above assumptions and some of the evidence upon which they are based will now be discussed.

Postulate 1.—It is usually accepted from the earlier work of Fischer [4] and Willstätter, Kuhn, and Sobotka [5] that the nature of the aglycon has only a quantitative effect on the rate of enzymic hydrolysis of a glycoside. Probably the best argument for this assumption is the great number of β-glucosides which have been prepared by Fischer, Helferich, Veibel and others, all of which have been found hydrolyzable by almond emulsin. An important exception occurs when the aglycon is a sugar, since there are numerous claims that fungal enzymes hydrolyze maltose but not methyl α-glucoside.[6] However, none of these experiments can be said to be in contradiction to the assumption made, since the preparations were relatively inactive, and in most instances a difference of 100 times in the relative rates of hydrolysis would hardly have been detectable. Since the various α-*D*-glucosides under standard conditions show a variation in the rate of hydrolysis, according to the nature of the aglycon group, of more than 40,000,[7] conditions must be chosen for the testing of the action against maltose and methyl, or preferably phenyl α-*D*-glucoside, such that comparable differences of specificity may be observed.

The experiments of Hestrin [8] are in more direct contradiction to this postulate. It was found that heat destroyed the ability of *A. oryzae* emulsin (Takamaltase) to hydrolyze sucrose and methyl α-*D*-glucoside under conditions such that the maltose hydrolyzing ability was not greatly affected. Since both sucrose and methyl α-glucoside are believed to have α-glucosidic linkages, this work must stand in contradiction to the postulation made, although two possible explanations may be given. The observed hydrolysis of methyl α-glucoside by the unheated enzyme was very small (2 percent after 24 hours), and this may have been so close to the experimental error that a slight destruction of the enzyme would make the hydrolysis less than the experimental error. Secondly, as suggested by Hestrin, the emulsin may contain several enzymes of the α-glucosidase type of variable heat resistance. The latter explanation is particularly necessary to explain the loss of sucrose inversion power.

Postulate 2.—There is practically universal agreement that hydrolyzable glycosides, which differ in the configuration of the glycosidic carbon, e. g., methyl α- and β-glucosides, require different enzymes. This was established by the work of Fischer.[9] Almond

[4] E. Fischer, Z. physiol. Chem. **26,** 60 (1898); **107,** 176 (1919).
[5] R. Willstätter, R. Kuhn, and H. Sobotka, Z. physiol. Chem. **129,** 33 (1923).
[6] H. Pringsheim, H. Borchardt, and F. Loew, Z. physiol. Chem. **202,** 23 (1931); K. Myrbäch, Z. physiol. Chem. **205,** 248 (1932).
[7] B. Helferich, Ergebn. Enzymforsch. **7,** 83 (1938).
[8] S. Hestrin, Enzymologia **8,** 193 (1940).
[9] E. Fischer, Ber. deut. Chem. Ges. **27,** 2985 (1894).

emulsin can hydrolyze both α- and β-galactosides, but it has been demonstrated that two enzymes are required. [10]

Postulate 3.—Fischer's work led him to believe that yeast and animal α-glucosidases were different.[11] With the notable exception of Weidenhagen, most workers in the field have accepted the conclusion that enzymes catalyzing the same reactions but from different sources are different, and considerable experimental evidence is available to prove the point.[12]

Helferich has expressed the opinion that there may be only two enzymes of each type[13], but such a limitation of the number requires a great deal of additional work before it can be accepted.

Postulate 4.—The investigation of the effect of substitution in the pyranose ring on the enzymic hydrolysis of the glycoside has been devoted almost exclusively to the glucoside series and to the hydrolysis by the β-glucosidase of almond emulsin. Helferich's results lead to the conclusion that the substitution of one or more hydroxyls of carbons, 2, 3, and 4 of a β-*D*-glucoside by methoxyl and tosyl groups makes the glucoside unhydrolyzable.[14]

Postulate 5.—Influence of Ring Type.—Although almond emulsin hydrolyzes β-glucopyranosides, the furanosides are not affected.[15] Similarly, invertase (fructofuranosidase) hydrolyzes fructofuranosides, but not the known fructopyranosides.[16]

D,L Specificity.—The available evidence indicates for all of the substances studied that a change in the configuration of *all* the asymmetric carbons in the molecule of a hydrolyzable glycoside (a change from the *D* to the *L* series) produces an unhydrolyzable glycoside. The best example is given by a pair of *D* and *L*-arabinosides.[17] Although both of the phenyl β- and α-*L*-arabinosides are hydrolyzed by the enzymes of almond emulsin (probably by the α- and β-galactosidase) the mirror images, the *D*-arabinosides are virtually unaffected. This is in agreement with the earlier results of Fischer on the *D*- and the *L*-glucosides [18] and with those of Helferich, Günther and Pigman [19] for the β-*D*-xylosides and the β-*L*-xylosides.

Sugar Specificity.—Changes of configuration of carbons 2, 3, and 4 of the hexosides produce the various hexose sugar types.[20] The enzymes in almond emulsin do not hydrolyze appreciably the methyl *D*-gulosides [21] and phenyl α-*D*-taloside.[22] Thus, changes in the configuration of a single carbon changes the glycoside from a hydrolyzable to an unhydrolyzable type, e. g., the mannosides and the talosides differ in the configuration of only a single carbon, carbon 4.

[10] B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Günther, Z. physiol. Chem. **208,** 91 (1932); W. W. Pigman, Z. physiol. Chem. **261,** 82 (1939).
[11] E. Fischer, Z. physiol. Chem. **26,** 60 (1898).
[12] K. Hill, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **86,** 115 (1934); B. Helferich and F. Vorsatz, Z. physiol. Chem. **237,** 254 (1935); E. Hofmann, Biochem. Z. **285,** 429 (1936); T. Miwa, C. Cheng, M. Fujisaki, and A. Toishi, Acta Phytochim. (Japan) **10,** 155 (1937); R. Weidenhagen and A. Renner, Z. Ver. deut. Zucker-Ind. **86,** 22 (1936); W. W. Pigman, J. Research NBS **30,** 159 (1943) RP1526.
[13] B. Helferich, W. Richter, and S. Grünler, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **89,** 385 (1937).
[14] B. Helferich and S. Grünler, J. pract. Chem. **148,** 107 (1937); B. Helferich and O. Lang, Z. physiol. Chem. **216,** 123 (1933); J. prakt. Chem. **132,** 321 (1932); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64,** 374 (1942).
[15] E. Fischer, Ber. deut. chem. Ges. **47,** 1980 (1914).
[16] R. Weidenhagen, Z. Ver. deut. Zucker-Ind. **82,** 921 (1932).
[17] B. Helferich, H. Appel, and R. Gootz, Z. physiol. Chem. **215,** 277 (1933); B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Günther, Z. physiol. Chem. **208,** 91 (1932).
[18] E. Fischer, Ber. **27,** 2985 (1894).
[19] B. Helferich, E. Günther, and W. W. Pigman, Ber. deut. chem. Ges. **72,** 1953 (1939).
[20] H. S. Isbell and W. W. Pigman, J. Research NBS **18,** 141 (1937) RP969; H. S. Isbell and H. Frush, J. Research NBS **24,** 125 (1940) RP1274.
[21] B. Helferich, W. W. Pigman, and H. S. Isbell, Z. physiol. Chem. **261,** 55 (1939).
[22] W. W. Pigman, J. Research NBS **26,** 197 (1941) RP 1369.

In general, it seems probable that each of the hexose types requires a special enzyme. The principal evidence opposed to this generalization is that in spite of considerable work to settle the question, Helferich [23] has never been able to separate the β-glucosidase and the β-galactosidase activities of almond emulsin. However, in alfalfa emulsin (lucerne emulsin), a β-galactosidase is present, although the β-glucosidase activity is small.[24] A possible explanation of Helferich's results is, that a single enzyme molecule may catalyze different reactions but that active areas or groups in different portions of the molecule may be responsible, so that while the enzyme is the same the activities may be ascribed to different portions of the molecule.

Postulate 6.—Changes remote from the ring usually produce only secondary effects on the rate of hydrolysis. The effect of the structure of the aglycon has been discussed (postulate 1). Substitution at the primary alcoholic group is another possibility, which has received attention by Helferich, but the data are available only for the glycosidases of almond emulsin. Substitution of various groups or atoms for the hydroxyl of carbon 6 of β-*D*-glucosides affects the rate of hydrolysis in measure dependent on the size of the substituent group[25] and similar effects are found for the *D-glycero-D-galacto*-aldoheptosides[26] (*D*-α-mannoheptosides), which are derivatives of the hydrolyzable *D*-galactosides in which a hydrogen of the primary alcoholic group has been replaced by a CH_2OH group.

When the primary alcoholic group is replaced by a hydrogen, a hexoside is converted to a pentoside, for example, glucose is changed to xylose, and the general conformation of the rings is usually similar in the two compounds. Although such changes may produce considerable effects on the conformation of the pyranose ring, the evidence indicates that enzymes hydrolyzing the hexoside also hydrolyze the corresponding pentoside. In all probability, β-glucosidase splits the β-glucosides and β-*D*-xylosides,[27] β-galactosidase the β-galactosides and the α-*L*-arabinosides,[28] and α-mannosidase the α-mannosides and the α-lyxosides.[29]

Postulate 7.—If the preceding postulates are correct, it would seem almost self-evident that naturally occurring enzymes would be only of the type to hydrolyze naturally occurring hexose *types*. Since *D*-gluosides and *D*-talosides are not known to occur in plant or animal materials, it appears improbable that special enzymes would be present in plant materials to hydrolyze these glycosides, and the previous evidence cited would eliminate the possibility of the hydrolysis of these substances by the known enzymes (β-glucosidase, β-galactosidase, α-mannosidase, α-galactosidase, and the other enzymes of the almond emulsin).

Postulate 8.—The thioglucosides are not hydrolyzed by the β-glucosidase of almond emulsin[30], but myrosin, an enzyme contained in black-mustard emulsin, hydrolyzes thioglucosides. Although there is not a great deal of information available on the *N*-glycoside hydrolyzing enzymes, almond emulsin does not hydrolyze nucleosides

[23] B. Helferich, Ergebn. Enzymforsch. **7**, 83 (1938).
[24] K. Hill, Ber. Verhandl. sächs. Akad. Wiss. Leipzig. Math. phys. Klasse **86**, 115 (1934).
[25] B. Helferich, S. Grünler, and A. Gnüchtel, Z. physiol. Chem. **248**, 85 (1937); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 374 (1942).
[26] W. W. Pigman, J. Research NBS **26**, 197 (1941) RP1369.
[27] B. Helferich and U. Lampert, Ber. deut. chem. Ges. **67**, 1667 (1934).
[28] B. Helferich, S. Winkler, R. Gootz, O. Peters, and E. Gunther, Z. physiol. Chem. **208**, 91 (1932); B. Helferich and U. Lampert, Ber. deut. Chem. Gesell. **68**, 1266 (1935).
[29] W. W. Pigman, J. Am. Chem. Soc. **62**, 1371 (1940).
[30] W. W. Pigman, J. Research NBS **26**, 197 (1941). RP1369.

(purine or pyrimidine *N*-glycosides), but enzymes are known[31] that will hydrolyze nucleosides. Since the nucleosides are usually *N*-ribosides or *N*-desoxyribosides, the nucleosidases might be expected not to hydrolyze *N*-glucosides. Until more information is available, these enzymes must be classified as separate groups of glycosidases.

The above assumptions are those on which the classification of the glycosidases depend. Most of these have fair experimental foundation, the main deficiencies being in the limited number of sources of enzymes which have been studied. The enzymes of almond emulsin have received considerable attention, and yeast invertase has been studied, but detailed evidence of the action of other enzymes is needed.

The preceding discussion brings up several other problems which cannot be answered at the present time but which ultimately may have to be considered. The polysaccharides, as emphasized by Weidenhagen in his original classification, are glycosides, and according to the first assumption, should be hydrolyzed by the same enzyme as that acting on the corresponding simple glycosides. Cellulase and β-glucosidase were considered by Weidenhagen to be the same, but the evidence which has accumulated indicates that the two are different. However, the question is still unanswered as to whether the cellulases may exert some slight activity for the hydrolysis of β-glucosides, and it may be that the two types of enzymes differ solely in their aglycon specificity.[32] In either case, from a practical standpoint, it seems desirable to classify carbohydrases hydrolyzing glycosides and oligosaccharides separately from the polysaccharidases although there may be a relationship between the classes of the type suggested by Weidenhagen. The possibility of special biosidases splitting the glycoside of a disaccharide into aglycon and disaccharide, has not been considered, since the literature on this subject is in a state of considerable confusion. Helferich and Weber[33] found no evidence for considering that the enzymes of almond emulsin hydrolyze the vanillin β-cellobioside and β-maltoside into vanillin and disaccharide in spite of earlier claims[34] to the contrary for the corresponding methyl derivatives. It seems probable, however, that certain emulsins may contain true biosidases and that when more work has been done, new classes of biosidases which hydrolyze the glycosides of disaccharides into *aglycon* and *disaccharide* may be necessary. An example of this type is the report that *Rubia tinctorum* emulsin (madder) hydrolyzes ruberytheric acid into 1,2-dihydroxyanthraquinone and 6-glucose β-D-xyloside (primeverose).[35]

Undoubtedly, other enzymes will have to be added to the list, since sugars of hexose types other than those upon which the classification is based are known to be naturally occurring. *L*-Rhamnose (*L*-mannosidases), *D*-ribose (*L*-talosidases, *D*-allosidases, *D*-ribosidases), and *L*-galactose (*L*-galactosidases) are some of the naturally occurring sugars for which it seems probable that corresponding enzymes exist. If the sugars of glycosides are formed in the plant by an irreversible process from another hexose type or by irreversible changes in the ring structure or configuration, then the corresponding enzymes may not be found. A possible illustration may be the re-

[31] H. Bredereck, Ergebn. Enzymforsch. **7**, 105 (1938).
[32] W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 369 (1942).
[33] B. Helferich and E. Weber, Ber. deut. Chem. Ges. **69**, 1411 (1936).
[34] E. Fischer and E. F. Armstrong, Ber. deut. Chem. Ges. **34**, 2896 (1901); **35**, 3154 (1902).
[35] D. Richter, J. Chem. Soc. (1936) 1701; see also, M. Bridel and C. Charaux, Pharm. Acta Helv. **1**, 107 (1926).

ported absence of enzymes in *Digitalis* and *Strophanthus* emulsins capable of hydrolyzing the digitoxose and cymarose glycosides from the same sources.[36]

Another possibility which is not considered is, that all of the enzymes may exhibit a slight but general nonspecific catalysis for the hydrolysis of glycosides and polysaccharides. In many instances where compounds are considered unhydrolyzable, small extents of hydrolysis close to the experimental error have been observed and in any case, "unhydrolyzable" means [37] an enzyme efficiency (Wertigkeit) of less than 10^{-5}.

2. POLYSACCHARIDASES

The classification of the polysaccharidases given in the second part of table 1 is not greatly different from that commonly accepted for this group of enzymes. That for the amylases follows Ohlsson and Gore,[38] and includes the results of more recent work, such as the possibility of a disaggregating amylophosphatase,[39] the production of Schardinger dextrins by *Bacillus macerans* emulsin,[40] and the discovery of amylolytic phosphorylases hydrolyzing certain starches and glycogen to glucose 1-phosphate.[41] The suggestions of Kertesz [42] are followed for the pectinases, and sufficient is not known to classify the other enzymes of this group in other than the conventional manner. It is believed, however, that enzymes such as cellulases and the various amylases also represent classes of enzymes rather than invariable individuals.

IV. NOMENCLATURE OF INDIVIDUAL ENZYMES

As mentioned previously[43], it seems advisable to restrict the term "emulsin" to mixtures of enzymes such as are obtained by extracting plants, animal organs, and microorganisms. The source is designated by an appropriate adjective, e. g., almond emulsin, yeast emulsin, etc. The main classes of glycosidic hydrolyzing enzymes are designated according to the alpha or beta hexose type involved, as α or β-hexosidases. In some instances it may be preferable to use other ring types, but hexose types should be used when possible. Since the enzymes generally act on the *D*-pyranosides, these designations are omitted from the name unless the furanose or "*L*" forms of the hexosides are involved.

The suggestion was originally made by Duclaux[44] that individual enzymes be named by adding the suffix "ase" to the name of the substrate. This has been done in the naming of the classes of glycosidases, but application to individual enzymes seems undesirable, since the action of none of the glycosidases known is limited to a single substrate and until all possible aglycon structures have been studied, it would not be known which is the most easily hydrolyzed.

[36] A. Stoll and J. Renz, Enzymologia **7**, 362 (1939).
[37] B. Helferich, H. Appel, and R. Gootz, Z. physiol. Chem. **215**, 277 (1933); W. W. Pigman and N. K. Richtmyer, J. Am. Chem. Soc. **64**, 374 (1942).
[38] H. C. Gore, Ind. Eng. Chem. **28**, 86 (1936); E. Ohlsson, Z. physiol. Chem. **189**, 17 (1930).
[39] E. Waldschmidt-Leitz and K. Mayer, Z. physiol. Chem. **236**, 168 (1935).
[40] E. B. Tilden, M. Adams, and C. S. Hudson, J. Am. Chem. Soc. **64**, 1432 (1942).
[41] C. S. Hanes, Proc. Royal Soc. (London), [B] **128**, 421 (1940); [B] **129**, 174 (1940); A. A. Green, G. T. Cori, and C. F. Cori, J. Biol. Chem. **142**, 447 (1942).
[42] Z. I. Kertesz, Ergeb. Enzymforsch. **7**, 83 (1938).
[43] W. W. Pigman, J. Research NBS **30**, 159 (1943) RP1526.
[44] E. Duclaux, Microbiologie, p. 141 (1883); quoted by J. B. S. Haldane, Enzymes, p. 192 (Longmans, Green & Co., London, 1930).

The classification of Tauber and Kleiner[45] of α-glucosidases as "*True α-glucosidases*" and "*pseudo-α-glucosidases*" may be objected to on the same basis as the Duclaux system. The classification of Tauber and Kleiner is explained in the following quotation: "In fact, however, there appear to exist two groups of maltases: one which splits α-methylglucoside and other α-glucosides as well as maltose rapidly, which we propose to name *true α-glucosidases;* the second group of maltases which hydrolyze maltose rapidly, but which act very slowly on some α-glucosides, and do not act on others at all. We suggest that the latter be called *pseudo-α-glucosidases.*" There seems to be no valid reason for not considering maltose as a true glucoside, except that carbohydrate chemists, for convenience, have usually placed it in a separate classification as a disaccharide. Also, in the β-glucoside series "true glucosides" (heterosides) are known which are hydrolyzed both more slowly and more rapidly than the disaccharide cellobiose, and additional investigation in the α-glucoside series would undoubtedly find the same situation there.

It is suggested that, until more information on the specificity of individual enzymes is available, the individual glycosidases be named according to their source and general type of action. For the polysaccharidases, for which still less information is available, the name can be based on the general type of action and the source. Some of the common enzymes would then be: sweet almond β-glucosidase, yeast fructofuranosidase (or yeast invertase), yeast α-glucosidase (yeast maltase), yeast α-galactosidase (yeast melibiase), wheat β-amylase, pancreatic α-amylase, *A. niger* cellulase, etc.

WASHINGTON, December 26, 1942.

[45] H. Tauber and I. S. Kleiner, J. Biol. Chem. **105**, 681 (1934).

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FURTHER EXPERIMENTAL STUDY OF BEATER PRACTICE IN THE MANUFACTURE OF OFFSET PAPERS

By Charles G. Weber, Merle B. Shaw, and Martin J. O'Leary

ABSTRACT

Seventy-three experimental papers have been made in the Bureau's experimental paper mill in studies to determine the relationship between the mechanical beating of the fibers and the properties of offset papers made from them. A previous publication [1] contains the data for the wood-fiber papers. The present article reports an extension of the work to include papers made of rag fibers, and mixtures of rag and wood fibers.

The rag fibers responded to beating differently in some respects than the wood fibers. Old rags withstood the prolonged beating required for the development of maximum strength and optimum formation without the adverse effects of such treatment noted in the preparation of wood fibers. All the rag-fiber papers had appreciably lower expansivity [2] than wood-fiber papers of corresponding bond strength, and the mixture of old-rag fibers with strong sulfite, in equal proportions, produced papers with folding endurance approaching the average for the two pulps. Papers made of the sulfite pulp and wood-fiber filler pulp in like proportions have been found to have fold values little above that of the weaker pulps.

The addition of clay filler to a sulfite paper lowered the expansivity in the machine direction but did not lower it appreciably in the cross direction.

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I. INTRODUCTION

For more than 10 years, the National Bureau of Standards and the Lithographic Technical Foundation have cooperated in research on the paper requirements of the offset lithographic process. After determing the properties of paper desirable for offset printing, papermaking studies were made to find how to obtain the properties. The

[1] J. Research NBS 28, 241 (1942) RP1455.

[2] All references to expansion in this paper pertain to moisture effects.

relationship between the beating of the fibers and the characteristics of papers made from them under controlled conditions was determined.

The experimental papers were made in the Bureau's experimental paper mill. The fibers studied comprised various types of commercial wood pulps, waste papers, and new and old rags, all of which were used singly and in combinations. The beating of the various fibers and selected combinations of them was subjected to controlled variations, and the resultant effects on the properties of the papers were determined by tests of the finished papers. The relationships thus obtained for the wood-fiber papers were published in a previous report.[3] Data on rag fibers and further data on some wood fibers are contained in this article, together with limited data on the effects of clay filler and some information on the application of the results to the printing of war maps.

The research on lithographic papers is carried on with the assistance of the Lithographic Technical Foundation, and the studies were planned with the counsel of an advisory committee of technical representatives of that organization, under the chairmanship of R. F. Reed, Director of Lithographic Research, University of Cincinnati.

II. PAPERMAKING EQUIPMENT

The experimental paper mill at the Bureau is provided with complete semicommercial equipment which is adapted to the experimental manufacture of paper under conditions simulating those of commercial manufacture. Descriptions and photographs of the equipment are contained in previous publications.[4 5 6] The equipment used in this investigation was essentially as follows: a 50-pound beater with copper-lined tub and manganese-bronze bars and plate, and equipped with one washing cylinder; a jordan refiner with bars of bronze and steel alloy; a four-plate, flat screen; and a 29-inch fourdrinier papermaking machine with a wire 33 feet in length, two presses, nine 15-inch dryers, a calender stack of seven rolls, and a reel.

III. FIBROUS RAW MATERIALS

Three commercial grades of rags were used, new white shirt cuttings, and two grades of old rags—old white shirt cuttings and "twos and blues." Half-stuff pulps were prepared from these rags by the conventional methods of cooking, bleaching, and beating. The properties of the pulps are given in table 1. The sulfite wood pulp included in the table is the pulp used in the rag-sulfite mixtures and in the sulfite papers made in the previous work, data for which are included in this paper for comparison.

[3] See footnote 1.
[4] Tech. Pap. BS **21**, 338 (1927) T340.
[5] BS J. Research **3**, 904 (1929) RP121.
[6] Paper Trade J. **89**, 19, 60 (1929).

TABLE 1.—*Chemical characteristics of fibrous materials used in experimental manufacture of offset papers*

Fibrous material	Alpha-cellulose [1]	Beta-cellulose [1]	Gamma-cellulose [1]	Pentosans	Copper number	Ash [2]	Resins [2]	Acidity of pulp (glass-electrode method)	
								Cold-water extraction	Hot-water extraction
	%	%	%	%		%	%	pH	pH
Sulfite wood pulp	84.8	1.8	13.4	2.8	2.0	0.2	0.3	5.9	5.5
Half-stuff from new white shirt cuttings	92.9	5.9	1.2	.....	0.4	.1	.2	6.5	6.6
Half-stuff from old white shirt cutting	89.8	9.1	1.1	.....	.3	.2	.2	6.5	6.6
Half-stuff from old "two's and blue's"	90.5	8.8	0.7	.....	.4	.2	.4	6.7	6.7
Soda wood pulp	67.5	28.8	3.7	15.4	3.2	.7	.2	8.6	7.4

[1] Based on total cellulose.
[2] On oven-dry basis.

IV. MANUFACTURE AND TESTING

1. BEATING PRACTICE AND MACHINE OPERATION

A series of papers was made from each selected fiber furnish with controlled variations in the beating. The procedure followed in furnishing the stock to the beater, except as otherwise noted, was as follows: The beater tub was partially filled with water, the pulp was added, and then sufficient water to obtain the desired concentration. The time required for furnishing was approximately 15 minutes. Data on the beating intervals, beater-roll settings, jordan settings, freeness of the stock at the completion of the beatings and at the head box, the distance the water was carried beyond the second slice on the paper-machine wire, and the shrinkage in width while drying are shown in table 2. The position of the beater roll is expressed as the number of turns above (+) or below (−) zero setting, which is the point of contact between the roll and the bedplate. One turn moves the roll 0.008 inch.

The freeness results in table 2 were obtained with a Williams precision freeness tester. This instrument consists of a graduated glass cylinder placed above a metal cone having a valve at the bottom. A No. 80 wire screen forms the bottom of the cylinder. To determine the freeness of stock, the apparatus is filled with tap water to the zero mark, which is slightly above the wire. One liter of the stock to be tested is poured into the cylinder, the valve is opened, and the time require for 1,000 ml of water to drain from the instrument is noted. Two sets of values, distinguished by the letters A and B, are reported. For the A values, samples containing 3 g of dry stock per 1,000 ml were added to the instrument, whereas the values for B are for actual concentrations in the cylinder of 3 g of dry stock per 1,000 ml of mixture.

TABLE 2.—*Data on beating and condition of stock for different types of furnishes*

Paper machine run number	Beater furnish: Fiber (pulp)	Rosin [1]	Alum [1]	Position of beater roll after beating time of—: 0.0 hr.[4]	0.25 hr.[5]	0.5 hr.	1.0 hr.	1.5 hr.	2.0 hr.	2.5 hr.	3.0 hr.	3.5 hr.
		% [2]	% [3]									
1243	100% sulfite wood pulp, no filler	1	1.0	+10	+10	+3	+3	+3				
1244		1	1.0	+10	+10	+3	+3	+2½	+2½	+2	+2	+1½
1245		1	1.0	+10	+10	+3	+3	+2½	+2½	+2	+2	+1½
1311	100% No. 1 white shirt cuttings	1	1.2	+10	+10	+5	+4½	+4	+3½	+3	+2½	+2
1310		1	1.2	+10	+10	+5	+4½	+4	+3½	+3	+2½	+2
1308	Old rags: 66⅔% No. 1 old white, 33⅓% twos and blues	1	1.2	+10	+10	+3	+1	0	−½	−½	−½	−½
1307		1	1.2	+10	+10	+5	+4½	+4	+3½	+3	+2½	+2
1306		1	1.3	+10	+10	+5	+4½	+4	+3½	+3	+2½	+2
1312	50% sulfite wood pulp, 50% old rags (twos and blues)	1	1.2	+10	+10	+3	+3	+3				
1313		1	1.2	+10	+10	+3	+3	+2½	+2½	+2	+2	+1½
1314		1	1.1	+10	+10	+3	+3	+2½	+2½	+2	+2	+1½
1339	100% sulfite wood pulp, 15% filler (clay) added			+10	+10	+3	+3	+2½	+2½	+2	+2	+1½
1340				+10	+10	+3	+3	+2½	+2½	+2	+2	+1½

Paper machine run number	Position of beater roll after beating time of—: 4.0 hr.	4.5 hr.	5.0 hr.	5.5 hr.	6.0 hr.	6.5 hr.	7.0 hr.	7.5 hr.	8.0 hr.	8.5 hr.	9.0 hr.	9.5 hr.	Freeness of stock at completion of beating: A	B	Jordan setting	Acidity at head box quinhydrone method	Freeness of stock at head box [6]: A	B	Sheet shrinkage in width as formed [7]	Distance water was carried beyond 2d slice [8]
																pH			%	*in.*
1243													9	10	+8	4.9	16	19	1.9	8
1244	+1½	+1	+1	+1									15	17	+8	4.9	33	39	2.5	13
1245	+1½	+1	+1	+½	+½	0	0	−½	−½	−1	−1	−1	63	74	+8	4.9	111	129	4.7	43
1311	+1½	+1	+½	+½									195	222	+8	5.2	480	620	3.8	72
1310	+1½	+1	+½	+½	0	0	0	−½	−½	−½			720	850	+8	5.3	1,080	1,220	4.7	[9]
1308													216	252	+8	5.0	500	630	2.5	[9]
1307	+1½	+1	+½	+½									203	242	+8	5.0	575	690	2.5	[9]
1306	+1½	+1	+½	+½	0	0	0	−½	−½	−½			550	630	+8	4.8	1,070	1,200	2.8	[9]
1312													59	70	+8	5.1	130	150	2.8	40
1313	+1½	+1	+1	+1									120	140	+8	4.9	210	245	3.1	60
1314	+1½	+1	+1	+½	+½	0	0	−½	−½	−1	−1	−1	330	385	+8	4.8	640	775	4.4	[9]
1339	+1½	+1	+1	+1									16	19	+8	5.1	42	49	3.1	12
1340	+1½	+1	+1	+½	+½	0	0	−½	−½	−1	−1	−1	68	81	+8	4.8	114	132	4.7	42

[1] Rosin size was added 1 hour and the alum ½ hour before stock was dropped to chest.
[2] Based on dry weight of the fiber.
[3] Based on dry weight of the fiber and rosin.
[4] Lighter-bar up.
[5] Lighter bar down.
[6] Williams precision freeness tester.
[7] Change in width of dried sheet as wound on reel from width when formed.
[8] Measurement indicates point at which drainage of water from table rolls stopped.
[9] To suction box.

Fifty pounds of pulp was furnished to the beater in each instance. The beaten stock was dropped to a chest and pumped in a continuous stream through the stuff box and jordan to the paper machine without the use of a machine chest. The stuff box was of the conventional regulating-box type, having a constant head over an adjustable orifice. Screen plates with 0.018-inch slots were used. The stock was maintained at 90° F±2° at the head box. Every effort was made to keep the entire machine operation the same for all of the runs, so that all of the differences found in the properties of the papers could be definitely ascribed to the controlled variations in beating.

2. TESTING

All the physical and chemical tests of the pulps and papers were made by the TAPPI methods except the following, for which no official methods were available.

The bond test was that of Sutermeister and Osgood.[7] This test is essentially one of measuring the force required to split paper when the stress acts perpendicularly to its surface.

The degree of curl was determined by the Carson [8] method, which measures the maximum angle of curl of a specimen when one side is in contact with water.

Smoothness was determined with the Bekk [9] instrument, and permeability to air was measured with a Carson Precision Permeability Tester,[10] which measures the rate of air flow through the paper per unit of area with a pressure difference of 1 g/cm².

The physical tests were made in an atmosphere of 65-percent relative humidity and 70° F because those conditions were standard when the study was initiated, and they were used for the remainder of the study to keep all the results comparable.

V. DESCRIPTION OF THE EXPERIMENTAL PAPERS

Papers were made with fibers from new rags; old rags; 50 percent of old rags and 50 percent of sulfite wood pulp; and sulfite wood pulp with 15 percent of filler (clay) added. The minimum, medium, and maximum beating treatments of 1½, 5½, and 9½ hours, respectively, as used on wood-fiber papers reported in the previous paper were followed, except that for the all-rag papers 3½ hours was selected as the minimum beating interval and 8½ hours as the maximum. The jordan was used as a mixer only.

The properties of the papers obtained from each furnish by different degrees of beating are contained in table 3. Included in this table are data on three sulfite papers made with minimum, medium, and maximum beating. These papers were reported in the previous publication [11] and are repeated here to facilitate comparison. Papers 1243, 1244, and 1245 are considered representative for sulfite papers made with different degrees of beating.

[7] Tech. Assn. Pap. **24**, 136 (1941).
[8] Paper Ind. Paper World **22**, 246 (June 1940).
[9] Paper Trade J. **94**, 41 (June 30, 1932).
[10] BS J. Research **12**, 567 (1934) RP681.
[11] J. Research NBS **28**, 241 (1942) RP1455.

TABLE 3.—*Properties of experimental offset papers* [1]

Paper machine run number	Fiber furnish (pulp)	Beating time	Jordan setting	Weight, 25×40 in. 500 sheets	Thickness	Density	Opacity, contrast ratio	Bursting strength	Ratio of burst to weight	Tensile properties: Breaking load, Mach.	Tensile properties: Breaking load, Cross	Tensile properties: Elongation at rupture, Mach.	Tensile properties: Elongation at rupture, Cross
		hr.		*lb.*	*in.*	*lb./ft.*³	%	*pt.*	%	*kg.*	*kg.*	%	%
1243	100% sulfite wood pulp	1.5	+8	56.1	0.0041	47.3	76	21	37	4.4	2.5	2.5	3.8
1244		5.5	+8	55.9	.0039	49.6	75	26	47	5.9	3.0	2.4	4.7
1245		9.5	+8	55.4	.0038	50.5	71	34	61	7.8	3.6	3.0	7.0
1311	100% new rags; No. 1 white shirt cuttings	5.5	+8	55.2	.0039	48.9	80	26	47	5.8	3.7	3.4	6.2
1310		8.5	+8	55.4	.0035	54.6	79	29	52	6.0	3.9	3.3	7.4
1308	100% old rags; 66⅔% No. 1 old white, 33⅓% twos and blues	3.5	+8	54.3	.0038	49.3	85	18	33	3.8	2.8	3.4	4.8
1307		5.5	+8	57.6	.0042	47.4	85	22	38	4.3	3.1	3.1	4.9
1306		8.5	+8	56.0	.0040	48.4	86	20	36	4.7	3.3	3.4	5.1
1312	50% old rags; 50% sulfite wood pulp	1.5	+8	54.3	.0038	49.4	83	21	39	4.7	2.4	2.7	4.3
1313		5.5	+8	54.3	.0038	49.4	81	24	44	5.4	2.9	2.4	5.6
1314		9.5	+8	54.9	.0035	54.2	79	27	49	6.2	3.4	3.3	7.1
1339	100% sulfite wood pulp with 15% filler (clay) added	5.5	+8	55.0	.0035	54.3	84	11	20	3.5	1.8	2.4	3.0
1340		9.5	+8	57.6	.0034	58.5	82	19	33	5.2	2.3	2.2	4.7

Paper machine run number	Tearing strength, Mach.	Tearing strength, Cross	Folding endurance (Schopper), Mach.	Folding endurance (Schopper), Cross	Expansion for a change of relative humidity of 15 percent, Mach.	Expansion for a change of relative humidity of 15 percent, Cross	Curl	Smoothness (Bekk)	Air permeability	Oil penetration	Sizing value (dry-indicator method)	Bond test
	g	*g*	*Double folds*	*Double folds*	%	%	*deg.*	*sec.*	*cm³/m²/sec. g/cm²*	*sec.*	*sec.*	*lb.*
1243	148	150	141	33	0.066	0.172	52	19	1,236	20	49	44.3
1244	126	144	390	58	.075	.207	60	20	570	32	51	55.7
1245	97	102	1,527	342	.091	.284	180+	17	52	195	58	85.8
1311	117	117	811	124	.062	.203	68	43	13	225	7	73.8
1310	95	100	656	180	.079	.288	180+	40	41	472	20	90.2
1308	57	55	16	13	.066	.151	43	45	129	83	10	76.3
1307	75	71	43	28	.060	.153	43	36	89	146	11	74.7
1306	63	62	26	28	.069	.177	60	38	58	184	11	83.6
1312	80	90	170	34	.070	.188	53	45	222	69	16	61.8
1313	83	87	297	71	.064	.199	65	47	107	124	15	70.9
1314	65	68	341	89	.079	.252	160	55	24	274	20	95.6
1339	130	128	18	9	.058	.179	45	28	580	40	25	40.8
1340	92	118	174	29	.067	.259	180+	36	91	120	24	65.5

[1] All the physical tests were made under conditions of 65-percent relative humidity and 70° F.

VI. INTERPRETATION AND DISCUSSION OF DATA

Relationships between some of the important properties of the finished papers are shown graphically in figures 1, 2, and 3. In these figures, the scales are so arranged that the data for the various properties are roughly comparable irrespective of their absolute values. For the properties for which low values are desirable, the scales are inverted so that, in all instances, a relatively high position on the scale indicates a high relative quality. The division into three classes is for ease of comparison and is strictly arbitrary.

Figures 1 and 2 show graphically the comparative properties of papers made from different fiber furnishes with like beating treatments. The beating for all papers shown in figure 1 was medium and for those in figure 2 was maximum. The effects of beating on the properties of papers made from sulfite and from old rags are shown in direct comparison in figure 3. The chart shows graphically how the two kinds of fibers respond differently to beating. With continued

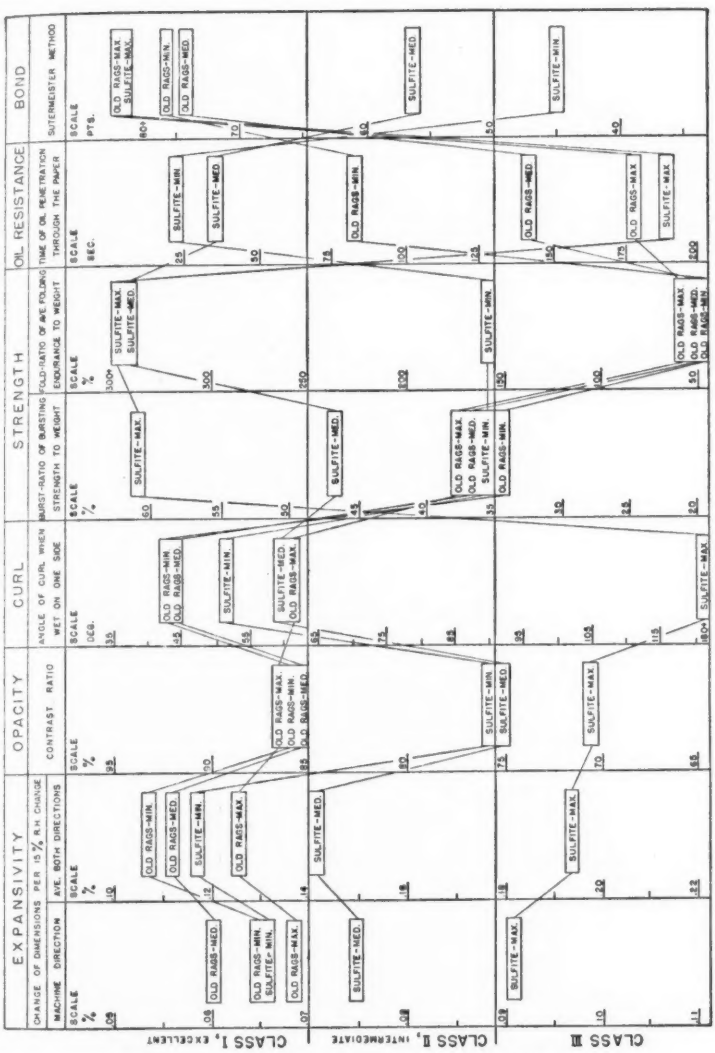

FIGURE 1.—*Relative properties of papers made with medium degree of beating from different fiber furnishes.*

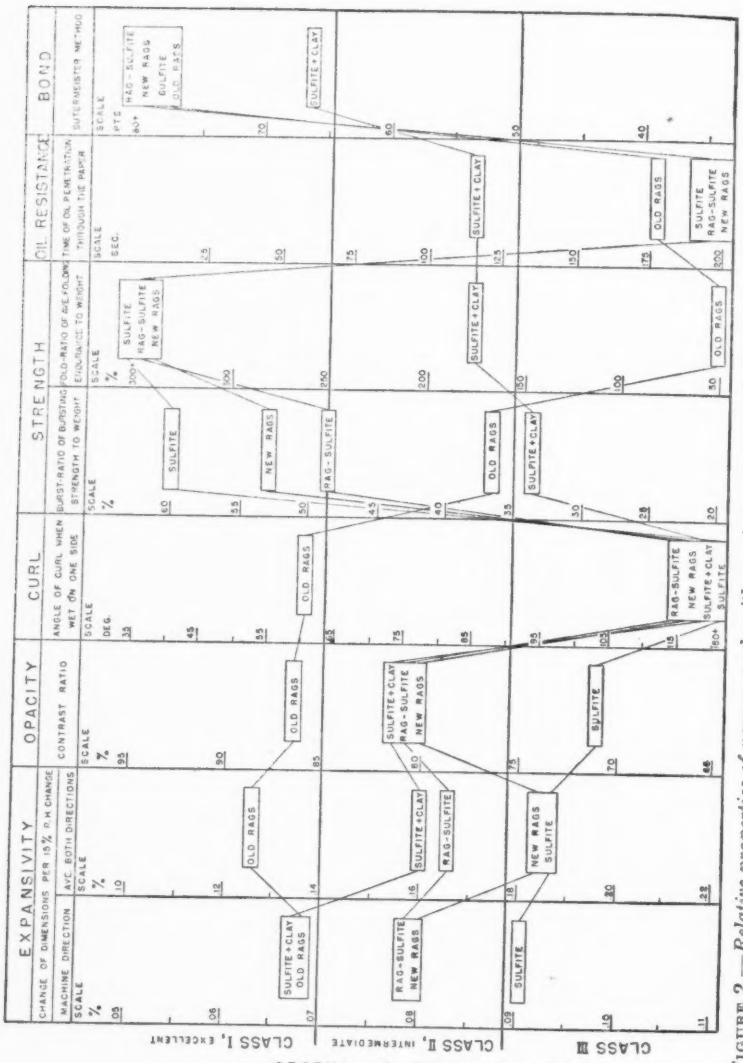

FIGURE 2.—*Relative properties of papers made with maximum degree of beating from different fiber furnishes.*

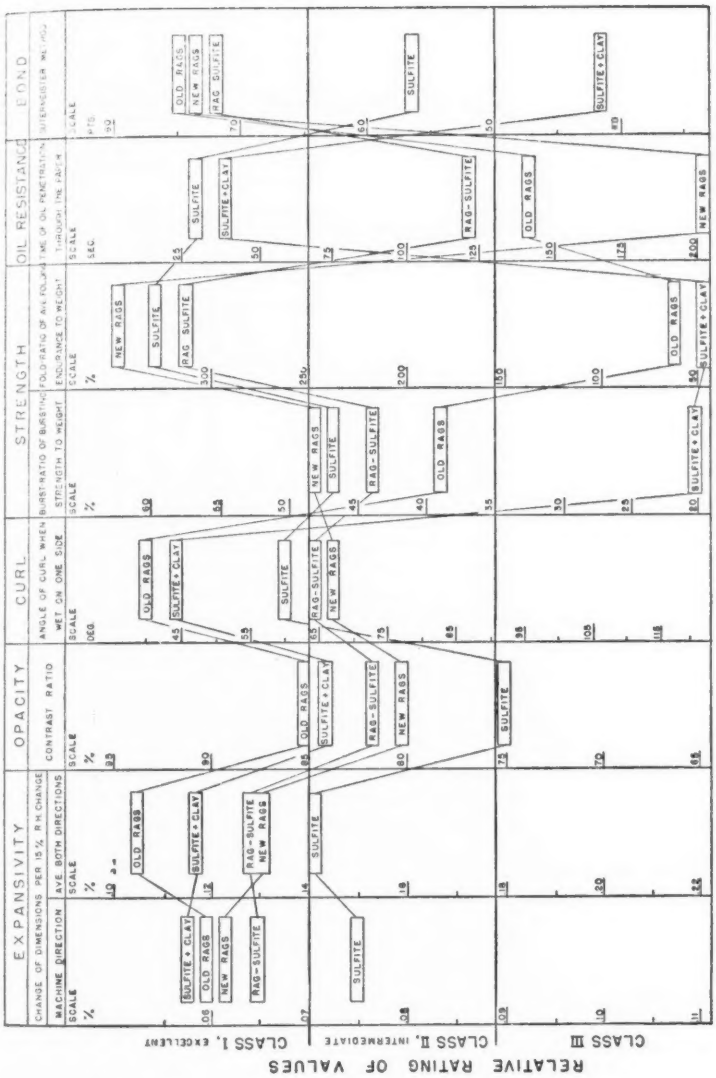

FIGURE 3.—*Relative effects of degree of beating on properties of papers made of sulfite wood fiber and of fibers from old rags.*

beating, the sulfite pulp develops high strength comparatively fast. However, the increased strength is accompanied by obvious effects of hydration, namely, increased expansivity, loss of opacity, and increased tendency to curl. The old-rag fibers show little hydration and apparently can be beaten to obtain the ultimate in formation and finish without the undesirable effects of hydration so apparent in the sulfite papers. The relative over-all effects of beating are shown in table 4. Here the papers included in figures 1, 2, and 3 are graded by an arbitrary scale of values, allowing 12½, 8, or 4 percent for each property for classes I, II, and III, respectively, so that a paper in class I for all properties would obtain a rating of 100 percent.

TABLE 4.—*Ratings of papers in figures 1 and 2.*

Fiber furnish	Rating values		
	Minimum beating	Medium beating	Maximum beating
	Percent	*Percent*	*Percent*
Sulfite wood fiber	78.0	73.5	57.5
New rags		78.0	65.5
Old rags	78.5	78.5	78.5
50% sulfite, 50% old rags	82.0	82.0	57.5
50% sulfite, 50% soda [a]	74.5	74.0	73.5
Sulfite, plus 15% clay filler		70.0	65.0

[a] Data from Research Paper RP1455.

In the work previously reported [12] for wood pulps, it was pointed out that a paper made of a mixture of wood pulps usually had a folding endurance little above that of the weaker pulp. That this did not hold for mixtures of sulfite wood pulp and old rags is indicated by the limited data reported in figure 4. The folding endurance of these mixtures approached the average for papers made from the individual pulps.

A relationship is known to exist between the amount of gel formed in beating or so-called hydration of wood pulp and the bond strength of the finished papers. This is because the gel is a cementing substance. However, in the beating of cotton-rag fibers, comparatively little gel is formed. Here the beating frays the ends of the fibers into fibrillas, which become interlaced in the formation of the paper to provide the bond strength without the cementing gel. There is no known method for measuring directly the gel formation or the proportion of the strength of a sheet that is derived from the fraying of the fibers. However, there is evidence to indicate that excessive hydration is associated with high expansivity, and figure 5 will be of interest in this connection. Here the relationships between bond strength and expansivity are shown. It will be noted that, in general, the expansion per unit of bond strength is appreciably higher for the wood-fiber papers than for the rag-fiber papers, which hydrate much less.

[12] J. Research NBS 28, 241 (1942) RP1455.

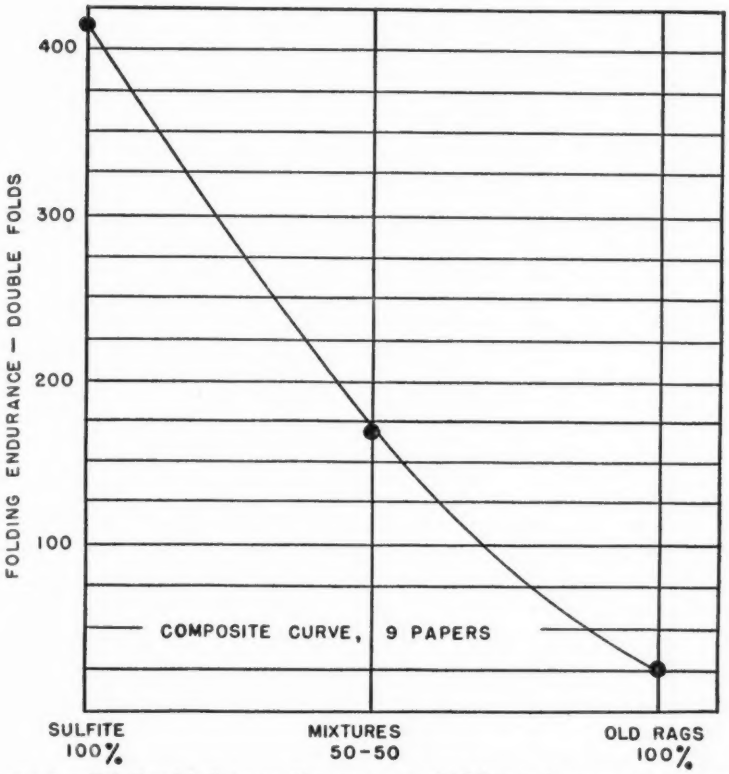

FIGURE 4.—*Relationship between fiber content and folding endurance of sulfite wood fiber, rag, and sulfite-rag papers.*

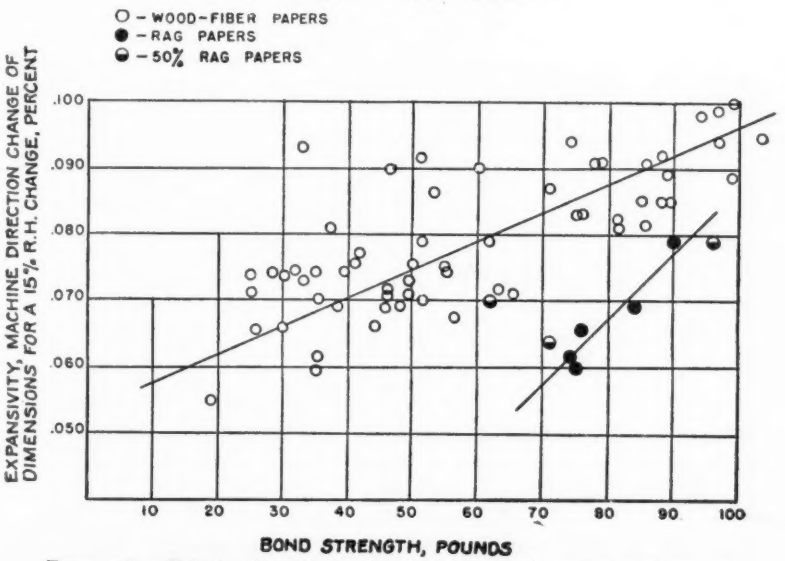

FIGURE 5.—*Relationship between bond strength and expansion of papers.*

VII. SELECTION OF OFFSET PAPERS FOR WAR MAPS

Most of the maps required for military purposes are printed by the offset lithographic process. Hence, it is of interest to consider the properties of offset papers with reference to their use in war maps. The performance of these maps is so important that printing quality can be regarded as secondary. Papers that are not satisfactory in the field should be eliminated from consideration, despite possible excellent lithographic quality. From a consideration of some of the uses of maps, it is believed that the base paper should have low expansivity, so that the maps will remain reasonably true to scale; relatively good resistance to tearing and surface abrasion, particularly when wet; flexibility to fold repeatedly without breaking; good writing quality for marking on with ink or pencil; and low gloss, to permit reading in bright sunlight. In addition, the paper must give sufficient contrast with the map colors for legibility under illumination of very low intensity, such as candlelight. Tendency to form deep creases when sharply folded or to retain permanent curl after rolling are objectionable characteristics.

Scale distortion resulting from humidity changes in the field are unavoidable, but they can be kept at the minimum by using a paper with low expansivity. If a map is printed true to scale in an air-conditioned plant at 50-percent relative humidity, it will be subject to a maximum humidity variation of 50 percent, plus or minus. Hence, theoretically, the expansion of the paper for a relative humidity change of about 50 percent should be not greater than the permissible scale error. For example, let us assume 60 yards in a range of 15,000 yards to be the maximum probable error in artillery firing practice. Expansion or contraction of the paper map of 0.5 percent would cause a scale error greater than the error in firing.

Thus a paper may have expansivity low enough for obtaining reasonably good register in printing and yet produce scale errors in the field due to distortion. The expansivity data in table 5 were obtained on map papers that gave no serious register difficulties, yet the possibility of scale error, unless corrections are applied to the measurements, are apparent. In an atmosphere of 95-percent relative humidity, the average expansion in the cross direction would be 0.72 percent, corresponding to an error of 108 yards in 15,000.

TABLE 5.—*Expansivity of some commercial map papers*

Paper number	1	2	3	4	5	Average
Expansion for a change of relative humidity of 15 percent:						
Machine (%)	0.05	0.06	0.07	0.07	0.08	0.065
Cross (%)	.30	.26	.20	.22	.23	.24

VIII. SUMMARY AND CONCLUSIONS

The rag fibers, particularly those from old rags, responded quite differently to beating than strong wood fibers. With the former, continued beating to develop strength, formation, and finish was not accompanied by adverse effects on expansivity, as was previously found to be true of sulfite and sulfate fibers.

The folding endurance of papers containing old-rag fibers and strong wood fibers in equal proportions was approximately the same as the average of the two pulps, whereas in the case of like mixtures of the same wood fibers with weak filler pulp, the folding endurance was approximately only that of the filler pulp.

The expansion per unit of bond strength of the sheet was appreciably lower for the rag-fiber papers than for wood-fiber papers.

In the production of and use of maps, hygroexpansion of the paper is potentially more serious as a cause of scale error than as a cause of misregister in printing.

WASHINGTON, January 29, 1943.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1533

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EFFECTS OF ADDED MATERIALS ON SOME PROPERTIES OF HYDRATING PORTLAND CEMENT CLINKERS

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ABSTRACT

Studies were made of the effects of added materials on the properties of a group of portland cement clinkers representing standard-portland, moderate-heat-of-hydration, high-early-strength, sulfate-resistant, and white cements. The materials used were gypsum, sugar, calcium chloride, TDA (grinding aid), tannic acid, triethanolamine, calcium acetate, and fluosilicic acid. The effects were judged by comparing the results of tests of specimens of clinker pastes containing the materials under investigation with the results of similar tests of the clinker pastes to which nothing had been added.

It was found that although some of the materials caused large changes in the behavior of the clinker pastes during their early history, these effects largely disappeared thereafter. Few of the substances had much effect on the results of tests performed at 28 days. No tests were made to evaluate the effect of the added materials after longer periods.

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I. INTRODUCTION

It is known that many properties of hydrating cements are affected differently by various added materials. That this is also true of commerical portland-cement clinkers [1] [2] is shown by recent studies [1] of the aqueous extracts of portland-cement-clinker pastes. The present paper is one of a series dealing with the results of these studies,

[1] To avoid confusion, it is to be noted that "clinker" refers to the ground product containing no added substance, whereas "cement" contains gypsum added during grinding.

[2] Figures in brackets indicate the literature references at the end of this paper.

and is, in part, concerned with the behavior of the pastes from which the filtrates discussed in the preceding paper [1] were removed. The properties investigated were the temperature-time relations and the heats of hydration of the clinker pastes, the strengths of mortar and concrete specimens fabricated from these pastes, the flows of the concretes, the sugar solubilities of the clinkers according to Merriman's procedure [2], and the amounts of floc developed by the clinkers when tested according to Paul's method [3]. The temperature-time curves, the results of the sugar solubility and floc tests, and part of the heats of hydration were determined, using pastes from which no filtrate had been removed.

II. MATERIALS

1. CLINKERS

To facilitate comparisons, the clinkers are given the same identification numbers in this paper as in preceding publications [1, 8]. The chemical analyses and computed compound compositions [4] of the 12 clinkers are given in table 1, together with the finenesses as determined by means of the Wagner turbidimeter [5]. Clinkers 1, 2, 3, 4, 6, 7, 11, and 12 were standard, portland-cement clinkers [6]. Clinker 3, although classified as standard-portland, was actually a high-early-strength-cement clinker, probably because of its greater fineness (2,260 cm^2/g, compared to the finenesses of 1,760 to 1,960 cm^2/g of the other clinkers). Clinkers 5, 8, and 9 were moderate-heat-of-hydration clinkers, and clinker 10 was a sulfate-resistant cement clinker.

TABLE 1.—*Analyses, calculated compound compositions, and fineness of ground cement clinkers*

Clinker	Chemical composition								Loss on ignition
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	
	%	%	%	%	%	%	%	%	%
1	23.9	5.6	3.4	64.6	0.6	0.56	0.05	0.09	1.1
2	24.9	0.5	4.2	64.1	.9	.04	.25	.00	5.3
3	22.0	2.5	5.7	67.6	1.1	.02	.11	.01	1.1
4	22.3	2.5	5.8	64.0	2.8	.09	1.32	.51	0.9
5	22.8	4.3	5.0	62.8	2.9	.05	1.05	.37	.9
6	22.1	2.5	5.4	64.7	2.6	.62	0.53	.18	1.3
7	21.7	2.2	6.8	65.2	2.7	.18	.18	.32	0.7
8	22.4	4.6	5.0	64.8	2.1	.17	.20	.30	.4
9	22.8	5.3	4.0	64.7	1.4	.87	.09	.35	.5
10	26.0	2.8	2.6	65.8	1.5	.13	.26	.12	.8
11	22.4	2.3	5.9	64.4	3.7	.43	.37	.12	.7
12	21.6	3.9	6.7	64.7	1.3	.12	.76	.28	.8

Clinker	Insoluble residue	Free lime	$3CaO.SiO_2$	$2CaO.SiO_2$	Calculated compound composition		Fineness
					$3CaO.Al_2O_3$	$4CaO.Al_2O_3.Fe_2O_3$	
	%	%	%	%	%	%	cm^2/g
1	0.3	0.1	50	31	0	17	1,760
2	.3	5.3	22	55	10	1	1,960
3	.3	0.7	63	16	11	7	2,260
4	.3	.4	47	29	11	8	1,850
5	.4	.2	42	34	6	13	1,830
6	.2	.9	52	24	10	8	1,780
7	.3	.8	50	25	14	7	1,840
8	.2	1.0	49	27	6	14	1,850
9	.5	0.1	55	24	2	16	1,850
10	.3	.8	45	40	2	9	1,820
11	.5	.4	47	28	12	7	1,910
12	.3	.7	46	27	11	12	1,820

Other characteristics of the clinkers were as follows: Clinker 2 was a white-cement clinker which contained 5.3 percent of free lime and had a loss on ignition of 5.3 percent. Clinkers 4 and 5 were the products of one manufacturer, and clinkers 7 and 8 were the products of another. Each of the remaining clinkers came from a different manufacturer.

Each clinker was ground to the fineness reported in table 1 and stored in an air-tight steel drum.

2. ADDITION AGENTS

The materials added were gypsum, calcium chloride, calcium acetate, sugar (sucrose), tannic acid, triethanolamine, TDA (grinding aid), and fluosilicic acid. The gypsum was a commercial mineral product, ground to pass a No. 200 sieve. Analysis showed that it contained 46.7 percent of SO_3 and had a loss on ignition of 20.1 percent. The TDA was described by its manufacturers as a mixture of "triethanolamine and highly purified soluble salts of modified lignin sulfonic acids." The remainder of the materials were commercial products of chemically pure quality. The quantities used and the methods of incorporating the added materials are shown in table 2.

TABLE 2.—*Addition agents, amounts used, and methods of incorporation*

Material	Amount	Methods of incorporation[a]
	Percent [b]	
Gypsum	3.75	I
Calcium chloride	[c]1.46	II
Calcium acetate	[c]1.35	II
Sugar	0.05	II
Tannic acid	.20	II
Triethanolamine	.10	II
Fluosilicic acid	[c].33	II
TDA	.033	IIA

[a] Methods of incorporation: I, The gypsum was mixed with the clinker for 2 hr in a ball mill with a few pebbles; II, these materials were added to the mixing water; and IIA, the TDA was added to the mixing water for the determinations of the time-temperature curves, the sugar solubilities, and the amounts of floc. For the remainder of the tests, it was dissolved in 7 times its weight of water, sprinkled on the ground clinker, mixed thoroughly in a ball mill, and the mixture allowed to stand for at least 24 hr before use.

[b] The gypsum added was 3.75 percent of the mixture, and the other materials were added in the amounts indicated as percentage by weight of the clinker.

[c] Anhydrous basis.

III. PROCEDURE

1. TEMPERATURE CHANGES OF PASTES

Determinations of the temperature changes of the pastes were made, using mixtures of 200 g of clinker and 70 g of water (C/W ratio=2.86). The pastes, contained in small tin cans, were mixed for 1 min with a high-speed motor-driven stirrer. Copper-constantan thermocouples were inserted in the pastes, and the cans were sealed and placed in stoppered vacuum flasks in a cabinet maintained at 25.0±0.1° C. Frequent measurements of the temperature of the pastes were obtained by connecting the thermocouples to a six-point recording potentiometer. Details of the test and a description of the apparatus have been published [7, 9.]

2. CONDITION OF THE PASTES

Qualitative observations were made of the consistencies of the pastes during mixing and before and after remixing at 2 hr.

3. HEATS OF HYDRATION

Two procedures were used in determining the heats of hydration. The heat evolved at 12 and 24 hr was estimated from the temperature changes of the pastes as described in the following paragraph. The heats of hydration at 7 and 28 days were determined by the heat-of-solution method.

The areas under the curves obtained by plotting the temperatures of the pastes against time were measured with a planimeter for the 12- and 24-hr periods. An average value of 0.0675 cal/hr deg g of cement, determined experimentally, was used to calculate the heat lost from the samples of clinker pastes. To the heat thus removed was added the heat stored in the paste by reason of its elevated temperature. The sum of the heat capacities of the cement and water in the paste was used as the heat capacity of the sample. This value, 0.55 cal/deg g, is somewhat higher than the value 0.41 cal/deg g for a well-aged paste obtained by interpolation of the data of Carlson and Forbrich [10]. No account was taken of the heat capacity of the inside of the vacuum flask and the sample container, since nothing was known of the temperature distribution between the thermocouple and the constant-temperature chamber in which the flask was placed. It was estimated that the heat capacity thus neglected was 0.1 to 0.2 cal/deg g of cement.

In determining the heats of hydration by the heat-of-solution method, the procedure described in Federal Specification SS–C–158a was followed with the exception of the method of preparing the paste samples. Large batches of paste (7,000 g of clinker plus 2,450 g of water, C/W=2.86) were prepared for the filtrations [1, 8] and samples taken as follows: (1) immediately after mixing, (2) from the same batch after filtration at 7 min, (3) after a paste, the duplicate of that filtered at 7 min, had aged for 1 hr 55 min (hereafter designated as 2-hr paste) and had been remixed, (4) after filtration of the 2-hr paste. The C/W ratio of the filtered pastes was restored to 2.86 by the addition of water before the samples were taken. The paste samples were stored in sealed vials at 21° C and tested at 7 and 28 days.

In most of the tests the heat of solution of the dry mixture of the clinker and the added material could not be determined directly. Consequently, it was calculated in all tests. The heats of solution and the losses on ignition were determined separately, both for the clinkers and for the materials investigated. Then for each mixture the contribution of each component to the heat of solution and to the residue on ignition was calculated. The ratio of total heat of solution to the total residue was then calculated and taken as the heat of solution of the mixture on an ignited basis. The heat of hydration of the hydrated paste was determined by subtracting its heat of solution from the value thus obtained.

4. STRENGTH TESTS

The specimens for the strength tests were fabricated by adding aggregates and water to portions of the filtered paste remaining after

the heat-of-hydration samples had been taken. No test pieces were made from unfiltered pastes. After fabrication, all specimens were stored at 21° C for at least 24 hr in a damp closet having a relative humidity of about 95 percent, and then in water at 21° C until tested. The specimens which had no strength at 24 hr were kept in the damp closet for 3 days. The strengths were determined at 1, 3, 7, and 28 days.

The tensile strengths were determined on briquets fabricated from mortar obtained by adding sufficient standard Ottawa sand (20 to 30 mesh) and water to a portion of the paste to give a 1:3 cement-sand mix having a C/W ratio of 2.40.

Compressive strengths were determined on 2-in. cubes made from (a) the same mortar mixture that was used for the briquets and, (b) a concrete mix. The latter was a 1:3½:3½ cement:fine aggregate: coarse aggregate mix with a C/W ratio of 1.25 by weight, in which 20 percent of the fine testing sand (Federal Specification SS–C–158a, paragraph F–4m (1)) was replaced by finely ground potter's flint. The coarse aggregate was the portion of Potomac River gravel passing the ⅜-in. sieve and retained on the No. 4.

The strength specimens were fabricated by a single operator. The concrete specimens were made first, followed in order by the briquets and the mortar cubes. This procedure resulted in the elapse of considerable time between the preparation of the pastes and the fabrication of the briquets and mortar cubes. The pastes were either ½ or 2½ hr old when received by the operator. Many of the pastes were rather stiff, and the test pieces could not be fabricated properly. For this reason, the most reliable results are those obtained for concretes made of the ½-hr pastes.

5. FLOWS (CONSISTENCIES)

The consistencies of the concrete mixtures were obtained according to the procedure given in Federal Specification SS–C–158a, paragraph F–4m (4).

6. MERRIMAN SUGAR SOLUBILITIES

The sugar solubilities were determined according to Merriman's procedure for cements [2] as follows: Fifteen g of clinker and 100 ml of a 15-percent sucrose solution were mixed mechanically for 2 hr. The mixture was then filtered, and 25 ml of the filtrate was titrated with 0.5 N HCl. The "end point" was shown by the color change of phenolphthalein, and the "clear point," if the solution was turbid, was obtained by the further addition of acid until turbidity disappeared.

7. PAUL FLOC TESTS

The amounts of floc developed were determined according to Paul's procedure [3] as follows: One gram of ground clinker was mixed with 100 ml of distilled water in a Nessler tube, and the tube was stoppered and placed in a horizontal position. The relative amount of flocculent precipitate ("none," "small," etc.) at 7 days was observed and recorded. The precipitate was then filtered off, ignited, and weighed. The amount of floc was reported as a percentage of the total weight of clinker originally taken.

IV. RESULTS AND DISCUSSION

1. TEMPERATURE-TIME CURVES, CONDITION OF THE PASTES, AND FLOWS

The temperature changes of the pastes, their observed condition during the first 2 hr, and the flows of the concretes all help to portray the behavior of the hydrating clinkers during their early history, and are therefore grouped together in the discussion.

Figure 1 presents the temperature changes with time of the pastes, with and without additions, during 24 hr or more after mixing. Figure 2 shows, on an enlarged scale, the temperature changes occurring during the first 3 hr. The effects of the various materials are indicated by alteration of the temperatures attained 15 min after mixing the pastes and by changes of the maximum temperatures attained, as well as the times at which they occurred.

In table 3 are listed qualitative observations of the condition of the clinker pastes at various times. The consistency of the concretes, presented as percentage flow in table 4, may also be taken as indicative of the progress of setting, since the pastes from which the specimens were fabricated were about ½ and 2½ hr old at the time the measurements were made.

In the following discussion when the statement is made that a substance changed the behavior of a paste, it is to be understood that the change is in comparison with the behavior of the clinker paste alone. No attempt will be made to discuss the behavior of individual clinkers, since detailed information may better be obtained from the tables and curves. There were occasional or even frequent exceptions to the statements made hereafter, but, in general, the effects of the additions were as described in the following paragraphs.

Gypsum reduced the initial temperatures of the pastes as well as the temperatures attained during the first 3 hr. The maximum temperatures, however, were increased frequently by rather large amounts, and the times required to reach the maximum temperatures were reduced in many instances. The lower temperatures attained during the first 3 hr were accompanied by increases in the fluidities of many of the pastes. Increased flows were observed for the concretes made from many of the clinkers. Certain of the clinkers exhibited quick-setting, which was eliminated by the addition of gypsum.

Sugar increased the temperatures attained in 15 min by nearly all the clinkers, but for many of the clinkers also increased the time required to reach the maximum temperatures. The quick-setting which some of the clinkers exhibited was retained, and this was caused in one case when sugar was added. Sugar also increased the flows of the majority of the concretes.

Calcium chloride caused a decrease in the initial temperatures of seven of the clinker pastes and an increase in the initial temperatures of the remainder. Shortly thereafter, however, the temperatures increased rapidly, and at the end of 3 hr the temperatures of the pastes containing calcium chloride were from 5° to 50° C higher than those of the clinker pastes alone. Calcium chloride eliminated the quick-setting exhibited by five of the clinkers. The flows at ½ hr were increased for nearly all of the clinkers, but at 2½ hr the flows were increased for only four of the clinkers and decreased for all but one of the remainder.

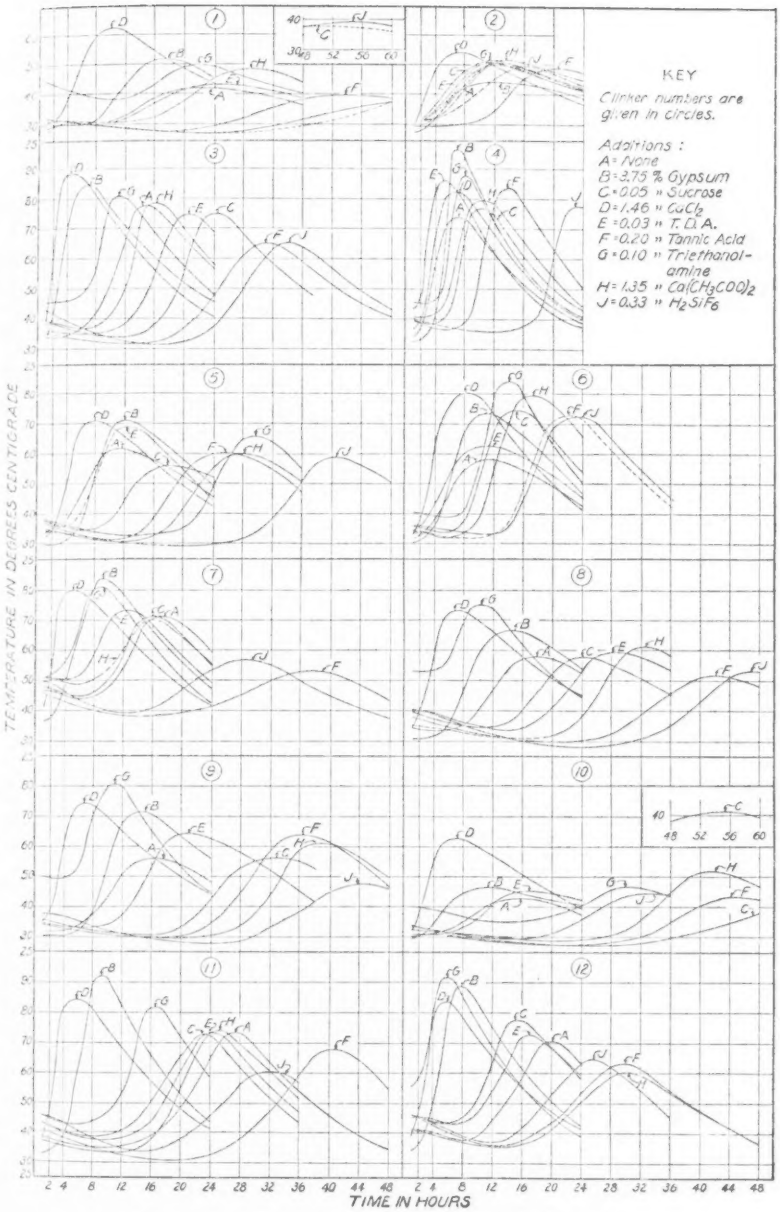
KEY
Clinker numbers are given in circles.
Additions :
A = None
B = 3.75 % Gypsum
C = 0.05 " Sucrose
D = 1.46 " $CaCl_2$
E = 0.03 " T. E. A.
F = 0.20 " Tannic Acid
G = 0.10 " Triethanolamine
H = 1.35 " $Ca(CH_3COO)_2$
J = 0.33 " H_2SiF_6
TEMPERATURE IN DEGREES CENTIGRADE
TIME IN HOURS

FIGURE 1.—*Temperatures of hydrating clinker pastes.*

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TDA increased the temperatures attained at 15 min for nearly all the clinkers. With a few exceptions, the maximum temperatures of the pastes containing TDA were equal to or only slightly greater than the temperatures attained by the clinker pastes containing no added material. For the majority of the clinkers the times required to reach the maximum temperatures were only slightly changed.

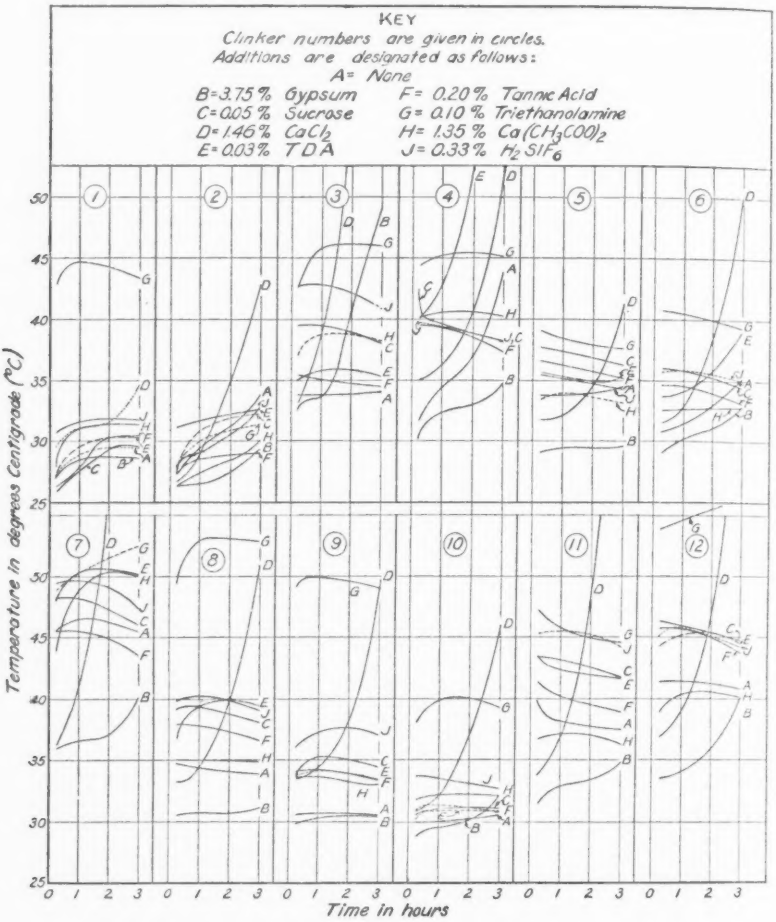

FIGURE 2.—*Temperatures of hydrating clinker pastes during first three hours after mixing.*

TDA eliminated quick-setting and reduced the stiffening of the pastes in most instances. This behavior is also indicated in the data of table 4 where the flows of the concretes containing TDA gave the highest averages both at ½ and 2½ hr. With the exception of the effects on the time-temperature curves, many of these changes may have been caused, at least in part, by prehydration, since the TDA was added to the ground clinkers as an aqueous solution 24 hr before the tests were begun.

TABLE 3.—*Condition of cement clinker pastes at various times with and without added materials*

Clinker	Time	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
1	During mixing	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid.
	At 2 hr	Soft	Soft	Soft	Stiff	Soft	Soft	Hard [a]	Sticky	Stiff.
	After remixing at 2 hr	Fluid	Plastic	Fluid	Plastic	Fluid	Fluid	Plastic	Fluid	Fluid.
2	During mixing	do	Fluid	do	Fluid	do	do	Fluid	do	Do.
	At 2 hr	Stiff	Soft	Slightly stiff	Slightly stiff	Soft	Stiff	Soft	Soft	Soft.
	After remixing at 2 hr	Plastic	Fluid	Sticky	Plastic	Fluid	Fluid	Fluid	Fluid	Fluid.
3	During mixing	Soft	do	Fluid	Fluid	do	*Quickset*	Quickset	do	Do.
	At 2 hr	Stiff	Hard	Slightly stiff	Hard		Soft	Hard	Stiff	Stiff.
	After remixing at 2 hr	Plastic	Plastic	Fluid	Plastic	Fluid	Fluid	Plastic	Sticky	Fluid.
4	During mixing	Fluid	Fluid	Quickset	Fluid	do	Quickset	Quickset	Soft	*Quickset.*
	At 2 hr	Stiff	Soft	Stiff	Stiff	Soft	Stiff	Hard	Stiff	Hard.
	After remixing at 2 hr	Plastic	Sticky	Plastic	Plastic	Fluid	Plastic	Dry	Sticky	Sticky.
5	During mixing	*Quickset* [b]	Fluid	Quickset	Fluid	do	Quickset	Quickset	Fluid	Quickset.
	At 2 hr	Soft	Soft	Soft	Soft	Soft	Hard	Hard	Soft	Hard.
	After remixing at 2 hr	Sticky	Fluid	Sticky	Fluid	Fluid	Plastic	Plastic	Fluid	Plastic.
6	During mixing	Fluid	do	*Quickset*	do	do	Quickset	Quickset	do	*Quickset.*
	At 2 hr	Slightly stiff	Soft	Slightly stiff	Slightly stiff	Soft	Stiff	Hard	Soft	Hard.
	After remixing at 2 hr	Plastic	Fluid	Soft	Fluid	Fluid	Sticky	Plastic	Fluid	Plastic.
7	During mixing	Quickset	do	Quickset	do	do	Quickset	Quickset	do	Quickset.
	At 2 hr	Hard	Slightly stiff	Hard	Hard	Hard	Hard	Hard	Hard	Hard
	After remixing at 2 hr	Plastic	Soft	Plastic	Plastic	Soft	Plastic	Dry	Sticky	Plastic.
8	During mixing	*Quickset*	Fluid	*Quickset*	Fluid	Fluid	*Quickset*	Quickset	Fluid	*Quickset.*
	At 2 hr	Slightly stiff	Soft	Slightly stiff	Hard	Slightly stiff	Stiff	Hard	Soft	Stiff.
	After remixing at 2 hr	Plastic	Fluid	Fluid	Fluid	Fluid	Plastic	Dry	Plastic	Plastic.
9	During mixing	Fluid	do	do	do	do	Fluid	Quickset	Fluid	Fluid.
	At 2 hr	Slightly stiff	Soft	Soft	Stiff	Soft	Soft	Hard	Soft	Stiff.
	After remixing at 2 hr	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Plastic	Sticky	Fluid.
10	During mixing	do	do	do	do	do	do	Quickset	Fluid	Do.
	At 2 hr	Slightly stiff	Soft	Stiff	Stiff	Soft	Slightly stiff	Stiff	Soft	Soft.
	After remixing at 2 hr	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Plastic	Fluid	Fluid.
11	During mixing	*Quickset*	do	Quickset	do	do	Quickset	Quickset	Soft	Quickset.
	At 2 hr	Stiff	Soft	Stiff	Hard	Stiff		Hard	do	Stiff.
	After remixing at 2 hr	Plastic	Plastic	Plastic	Plastic	Fluid	Plastic	Plastic	Sticky	Plastic.
12	During mixing	Quickset	Fluid	Quickset	Fluid	do	Quickset	Quickset	Fluid	Quickset.
	At 2 hr	Hard	Slightly stiff	Hard	Hard	Slightly stiff	Hard		Stiff	Hard.
	After remixing at 2 hr	Plastic	Plastic	Plastic	Plastic	Plastic	Plastic		Sticky	Plastic.

[a] "Hard" in each case indicates that the material could be reworked only by vigorous hammering with a heavy steel tamper.

[b] The condition of the paste designated as "quickset" indicates that vigorous mixing was required to maintain plasticity, that noticeable heat was evolved and that there was a marked decrease in workability. There were different degrees of quick setting. The pastes showing quickset that could be eliminated by mixing without apparent decrease in workability are identified by italic type; no appreciable heat was evolved during the mixing of these pastes.

TABLE 4.—*Flows of concrete mixes with and without added materials at ½ and 2½ hr after initial mixing of cement clinker pastes*

Clinker	Age	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	hr	%	%	%	%	%	%	%	%	%
1	½	123	122	134	119	143	127	------	131	105
	2½	122	111	127	114	132	122	109	116	102
2	½	118	115	110	125	120	90	113	121	105
	2½	------	113	110	89	103	99	106	109	98
3	½	108	97	109	104	102	97	95	27	87
	2½	103	65	110	66	104	98	84	18	85
4	½	63	93	60	96	114	60	------	99	60
	2½	54	87	69	54	94	56	43	93	50
5	½	69	114	80	107	121	66	------	126	48
	2½	79	107	89	110	114	68	58	134	75
6	½	92	99	83	100	112	80	------	127	81
	2½	79	86	95	85	104	81	68	131	83
7	½	91	97	76	100	94	66	------	22	64
	2½	81	94	73	69	78	66	------	------	------
8	½	86	104	100	111	108	92	------	68	87
	2½	85	109	84	100	99	96	87	84	87
9	½	106	99	110	108	115	101	------	81	111
	2½	101	107	109	90	111	98	89	79	94
10	½	115	111	128	121	113	103	------	104	115
	2½	107	113	117	104	117	104	118	111	101
11	½	88	94	98	109	112	98	60	35	88
	2½	87	97	98	72	105	98	66	32	89
12	½	78	101	92	111	104	87	------	37	75
	2½	76	107	87	80	86	74	------	35	69
Average	½	95	104	98	109	113	89	89	82	86
	2½	89	100	97	86	104	88	83	86	85

Tannic acid increased the temperatures attained in 15 min by all but four of the clinker pastes. The maximum temperatures were increased for only three of the clinkers and were decreased or unchanged for the remainder. The times required to reach the maximum temperatures were increased. All but three of the clinker pastes stiffened more rapidly when tannic acid was used. The majority of the flows were affected only slightly or not at all.

Triethanolamine increased markedly the temperatures reached in 15 min and also increased the maximum temperatures attained. The times required to reach the maximum temperatures were decreased for six of the clinkers and changed only slightly or increased for the remainder. Ten of the clinkers showed quick-setting. The flows of nearly all the concretes were decreased. Two of the clinkers showed little change in the stiffness of the pastes and in the flows of the concretes. In some instances, the flows could not be determined when triethanolamine was added.

Calcium acetate either increased or decreased by a small amount the temperatures attained by the pastes at 15 min. The times required to reach the maximum temperatures were increased. Calcium acetate eliminated the quick-setting exhibited by five of the clinker pastes. In many cases the pastes became very sticky. The flows of the concretes made from six of the clinkers were decreased, whereas the remainder were either increased or not greatly affected.

Fluosilicic acid increased the temperatures attained at 15 min for nearly all the clinkers. The maximum temperatures were decreased for a majority of the clinker pastes, and the times required to reach the maximum temperatures were increased. Quick-setting was retained and, in two instances, was caused by fluosilicic acid. The flows of the concretes made from five of the clinkers were decreased, whereas the remainder were affected only slightly or not at all.

2. HEATS OF HYDRATION

The heats of hydration determined by the heat-of-solution method are given in table 5. Those determined from the time-temperature curves are included in table 6. The treatment of the pastes filtered at 7 min most nearly approximates that of the pastes for which the time-temperature curves were obtained. Accordingly, the heats of hydration at 7 and 28 days of the 7-min pastes sampled before filtration, were made a part of table 6.

It will be noted in table 6 that in 9 out of 108 cases the 1-day heat of hydration equals or exceeds the heat of hydration at 7 days. Each determination is subject to error, and the net effect of individual errors in the two determinations may occasionally cause the 1-day heat of hydration to appear to exceed that at 7 days when this does not actually happen. However, it may well be that the paste at an elevated temperature in the vacuum flask hydrates to a greater extent in 1 day than the corresponding paste, stored at 21° C, hydrates in 7 days.[3] In spite of differences between the two methods, it was felt that the approximate heats of hydration at ½ and 1 day were of sufficient interest to be included in the paper. The heats of hydration at ½, 1, 7, and 28 days have been calculated as percentages of the heat of hydration of the clinker without addition and are presented in table 7 and figure 3. In this manner the direct comparison of heats of hydration measured by different methods is avoided.

For convenience, the level of significance of differences in percentages taken from table 7 was arbitrarily set at 10 percent for the ½- and 1-day and at 5 percent for the 7- and 28-day heats of hydration, respectively. That is, if a material caused a change in the heat of hydration of less than ±10 percent at ½ and 1 day and ±5 percent at 7 and 28 days, it is stated in the discussion that no change occurred. Statistical investigation of the heats of hydration shown in table 5 and of other similar data obtained in this laboratory indicates that in these measurements differences of less than 4 cal/g are probably not significant. The reader should bear this in mind in studying table 5 for detailed information on the effects of various additions and the influence of filtration of the pastes at the two ages.

The behavior of the individual cements may be followed in the tables or traced in figure 3. There were occasional exceptions but, in general, the effects of the additions were as described hereafter.

Gypsum increased the heats of hydration at ½ day, sometimes by several hundred percent. At 1 day, two-thirds of the heats of hydration were increased by an average of 30 percent. The changes at 7 days were small, whereas at 28 days most of the heats of hydration were unchanged.

Sugar reduced the heats of hydration of half of the clinkers at ½ day by an average of 48 percent. On the other hand, three heats of hydration were increased by nearly the same amount. At 1 day, one-third of the heats of hydration were decreased by an average of 47 percent, and one-third were increased by about half as much. At 7 and 28 days a few more increases than decreases in the heats of hydration occurred, but the changes were small.

[3] The differences between the 1- and 7-day heats of hydration for the 9 cases were small except when TDA was used. In these two cases the differences may have been caused by the different methods of incorporating the TDA.

TABLE 5.—*Heats of hydration of cement clinker pastes with and without added materials*

Clinker	Age of hydrating paste	Sampled [a]	No addition Filtered at —		Gypsum Filtered at —		Sugar Filtered at —		Calcium chloride Filtered at —		TDA Filtered at —		Tannic acid Filtered at —		Triethanolamine Filtered at —		Calcium acetate Filtered at —		Fluosilicic acid Filtered at —	
			7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	Days		*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*
1	7	Bf	49	49	49	55	49	52	67	59	48	50	47	57	70	76	59	64	58	54
	7	Af	49	50	50	59	50	51	66	59	52	50	50	54	74	71	62	63	58	54
	28	Bf	72	75	73	67	74	74	76	68	73	78	67	75	81	78	87	85	74	72
	28	Af	72	76	69	65	72	74	72	68	68	71	67	75	77	78	85	84	75	72
2	7	Bf	45	47	42	49	48	50	41	43	46	49	41	50	52	56	50	62	60	57
	7	Af	42	43	39	48	43	46	39	39	43	48	41	45	53	53	55	55	57	54
	28	Bf	56	51	58	59	65	69	55	57	66	63	68	65	72	73	69	77	64	64
	28	Af	52	51	59	57	65	69	56	55	61	64	65	64	68	65	69	71	64	63
3	7	Bf	82	81	82	83	84	84	80	77	76	79	78	76	93	96	92	87	84	87
	7	Af	79	79	77	80	82	79	78	80	75	77	77	76	88	89	88	87	86	89
	28	Bf	105	98	107	102	92	100	91	95	99	93	97	100	103	102	105	99	102	101
	28	Af	101	96	96	96	95	99	88	92	96	96	94	94	101	99	102	98	100	100
4	7	Bf	70	66	67	68	79	75	62	65	71	69	75	72	.....	68	83	87	78	77
	7	Af	67	67	67	70	77	72	64	64	69	63	76	73	.....	70	83	82	81	79
	28	Bf	80	80	77	71	83	81	73	74	77	74	80	78	.....	81	89	90	84	82
	28	Af	82	80	77	73	82	81	74	73	71	71	82	80	.....	82	92	95	87	79
5	7	Bf	60	64	65	63	66	67	65	63	58	49	67	69	.....	71	58	67	61	69
	7	Af	63	66	65	62	69	63	66	63	53	52	66	67	.....	73	62	67	65	65
	28	Bf	68	71	69	69	77	73	67	67	70	70	82	80	.....	86	78	78	76	79
	28	Af	70	72	72	70	74	75	67	66	62	73	78	82	.....	87	80	80	83	83
6	7	Bf	53	52	60	59	63	64	66	63	45	52	67	66	.....	71	74	71	67	69
	7	Af	59	55	57	54	59	68	64	62	48	52	68	65	.....	72	77	77	70	71
	28	Bf	74	70	64	68	78	81	70	74	67	65	77	72	.....	79	82	81	79	73
	28	Af	76	73	66	68	81	82	72	71	66	68	79	76	.....	79	83	88	79	75
7	7	Bf	79	82	83	81	78	82	71	70	77	80	79	85	.....	.....	83	90	75	83
	7	Af	86	82	82	79	81	81	71	69	84	82	70	76	.....	.....	82	88	77	84
	28	Bf	89	92	90	92	97	96	89	87	96	92	92	92	.....	.....	99	94	96	97
	28	Af	88	94	88	91	97	97	91	85	97	95	98	97	.....	.....	98	95	96	97
8	7	Bf	61	62	60	57	54	63	64	68	49	55	68	60	.....	77	71	64	60	61
	7	Af	67	60	58	59	62	65	61	67	47	55	66	60	.....	74	69	69	59	62
	28	Bf	75	76	75	71	76	73	78	78	71	70	80	77	.....	87	90	87	78	72
	28	Af	76	77	72	69	78	77	79	77	75	72	82	77	.....	87	93	90	78	80
9	7	Bf	57	54	60	65	50	56	66	64	50	48	63	60	78	75	66	57	54	58
	7	Af	55	55	63	64	57	55	60	63	48	49	63	61	.....	74	68	63	57	60
	28	Bf	74	71	72	69	81	80	70	72	69	68	77	80	84	82	85	82	78	81
	28	Af	74	74	72	73	79	84	72	71	69	70	77	79	.....	82	83	85	81	81
10	7	Bf	41	43	45	45	37	45	53	56	41	46	45	49	61	65	60	58	52	53
	7	Af	45	45	46	49	42	46	54	52	39	40	50	53	.....	66	60	58	50	51
	28	Bf	61	60	61	59	62	62	65	67	60	59	65	66	76	77	72	75	72	70
	28	Af	64	63	61	61	62	66	65	63	57	61	65	64	.....	77	75	75	70	70

11	7	Bf	71	77	76	76	75	78	69	70	65	71	70	73	82	77	72	82	71	76
	7	Af	75	80	74	76	79	80	70	69	68	73	72	74	81	81	78	82	75	77
	28	Bf	89	85	92	88	92	91	79	80	89	93	93	92	95	94	96	97	100	97
	28	Af	90	91	85	89	90	92	77	77	88	91	91	92	97	88	98	97	99	100
12	7	Bf	79	77	78	80	79	82	72	73	76	82	80	80	--------	--------	80	80	83	83
	7	Af	77	77	82	77	80	79	72	69	77	82	79	81	--------	--------	79	79	82	76
	28	Bf	93	92	91	92	88	95	85	88	93	90	91	92	--------	--------	98	98	94	95
	28	Af	95	94	94	93	90	96	89	83	88	92	92	93	--------	--------	102	99	92	95

• Bf = Before filtration. Af = After filtration.

TABLE 6.—*Heats of hydration of cement clinker pastes with and without added materials.*[a]

Clinker	Age of hydrating paste	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	Days	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*
1	½	9	16	6	39	8	6	20	8	7
	1	27	38	8	51	26	10	43	26	8
	7	49	49	49	67	48	47	70	59	58
	28	72	73	74	76	73	67	81	87	74
2	½	24	19	25	31	26	8	28	24	25
	1	38	31	38	39	39	32	41	41	36
	7	45	42	48	41	46	41	52	50	60
	28	56	58	65	55	66	68	72	69	64
3	½	36	60	14	63	17	11	56	38	15
	1	68	72	63	65	86	24	61	67	24
	7	82	82	84	80	76	78	93	92	84
	28	105	107	92	91	99	97	103	105	102
4	½	48	58	50	57	57	47	58	56	16
	1	53	64	59	63	61	66	64	66	61
	7	70	67	79	62	71	75	-------	83	78
	28	80	77	83	73	77	80	-------	89	84
5	½	38	41	20	48	42	30	14	10	9
	1	54	69	48	59	56	44	32	35	13
	7	60	65	66	65	58	67	-------	58	61
	28	68	69	77	67	70	82	-------	78	76
6	½	35	48	46	58	42	11	52	25	13
	1	48	62	63	65	56	58	67	70	58
	7	53	60	63	66	45	67	-------	74	67
	28	74	64	78	70	67	77	-------	82	79
7	½	34	60	37	58	53	21	61	41	23
	1	69	72	68	66	70	33	70	70	47
	7	79	83	78	71	77	79	-------	83	75
	28	89	90	97	89	96	92	-------	99	96
8	½	21	35	15	51	16	12	57	11	14
	1	49	58	45	64	38	16	67	20	16
	7	61	60	54	64	49	68	-------	71	60
	28	75	75	76	78	71	80	-------	90	78
9	½	24	35	11	51	14	9	60	9	12
	1	45	61	24	63	53	16	68	13	13
	7	57	60	50	66	50	63	78	66	54
	28	74	72	81	70	69	77	84	85	78
10	½	16	23	6	41	15	6	16	8	8
	1	28	36	8	52	33	8	29	11	16
	7	41	45	37	53	41	45	61	60	52
	28	61	61	62	65	60	65	76	72	72
11	½	15	60	21	60	19	14	32	13	18
	1	48	68	66	68	62	19	72	54	35
	7	71	76	75	69	65	70	82	72	71
	28	89	92	92	79	89	93	95	96	100
12	½	23	60	38	60	32	19	62	16	20
	1	63	68	73	69	69	42	68	37	53
	7	79	78	79	72	76	80	-------	80	83
	28	93	91	88	85	93	91	-------	98	94

[a] The ½- and 1-day heats of hydration were determined by integrating the time-temperature curves. The 7- and 28-day heats of hydration are those determined by the heat-of-solution method, using the 7-min. pastes before filtration.

Calcium chloride increased the heats of hydration at ½ day, usually by even larger amounts than did gypsum. At 1 day, three-fourths of the heats of hydration were increased and none were decreased. At 7 days the increases were more frequent and somewhat larger than the decreases, whereas at 28 days half of the heats of hydration were decreased by calcium chloride by an average of 8 percent.

TDA tended to increase the heats of hydration at the early ages and to leave them unchanged or to decrease them later. With a few exceptions the changes were not large.

Tannic acid reduced nearly all the heats of hydration at ½ and 1 day, whereas at 7 and 28 days most of the heats were unchanged or increased. The decreases were frequently rather large, whereas the increases seldom exceeded 25 percent.

TABLE 7.—*Heats of hydration of cement clinker pastes containing added materials as percentages of the heats of hydration of the pastes without addition* [a]

Clinker	Age of hydrating paste	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	Days	%	%	%	%	%	%	%	%
1	½	178	67	434	89	111	222	89	68
	1	141	30	189	96	37	159	96	30
	7	100	100	136	98	96	143	120	118
	28	101	103	106	101	93	112	121	103
2	½	79	104	129	108	33	117	100	104
	1	82	100	103	103	84	108	108	95
	7	93	107	91	102	91	116	111	133
	28	103	116	98	118	121	128	123	114
3	½	167	39	175	47	31	156	105	42
	1	106	93	96	127	35	90	99	35
	7	100	102	98	93	95	113	112	102
	28	102	88	87	94	92	99	100	97
4	½	121	104	119	119	98	121	117	33
	1	121	111	119	115	124	121	124	115
	7	96	113	89	102	107	----------	119	111
	28	96	104	91	96	100	----------	111	105
5	½	108	53	126	111	79	37	26	24
	1	128	89	110	104	82	59	65	24
	7	108	110	108	97	112	----------	97	102
	28	102	113	99	103	121	----------	115	112
6	½	137	131	166	120	31	159	72	37
	1	129	131	136	117	121	140	146	121
	7	113	119	125	85	126	----------	140	128
	28	87	105	95	90	104	----------	111	107
7	½	177	109	171	156	62	180	121	68
	1	104	99	96	102	48	101	101	68
	7	105	99	90	98	100	----------	105	95
	28	101	109	100	108	103	----------	111	108
8	½	166	71	243	76	57	271	52	67
	1	118	92	130	78	33	137	41	33
	7	98	89	105	80	111	----------	117	98
	28	100	101	104	95	107	----------	120	104
9	½	141	46	212	58	38	250	38	50
	1	136	53	140	118	36	151	29	29
	7	105	88	116	88	110	137	116	95
	28	97	109	95	93	104	114	115	105
10	½	144	38	256	94	38	100	50	50
	1	129	29	186	118	29	104	39	57
	7	110	90	129	100	110	149	146	127
	28	100	102	107	98	107	125	118	118
11	½	400	140	400	127	93	213	86	120
	1	142	137	142	129	40	150	113	73
	7	107	106	97	92	99	116	102	100
	28	103	103	89	100	104	107	108	112
12	½	261	165	261	139	82	27	70	87
	1	108	116	110	110	67	108	59	84
	7	99	100	91	96	101	----------	101	105
	28	98	95	91	100	98	----------	105	101

[a] The ½- and 1-day heats of hydration were determined by integrating the temperature-time curves. The 7- and 28-day heats of hydration were determined by the heat-of-solution method, using the 7-min. pastes before filtration.

Triethanolamine increased most of the heats of hydration at all ages for which data were available. In several instances pastes containing triethanolamine hardened so rapidly that all tests were not performed. The few decreases in the heats of hydration that occurred were usually rather large.

Calcium acetate and fluosilicic acid decreased the majority of the heats of hydration at ½ and 1 day and increased them at 7 and 28 days. In general, the decreases were larger than the increases.

It may be noted that the effects of these substances were frequently large and variable during the first 24 hr, but that by 7 days most of the changes were small. At the end of 28 days very many of the heats of hydration were not affected significantly.

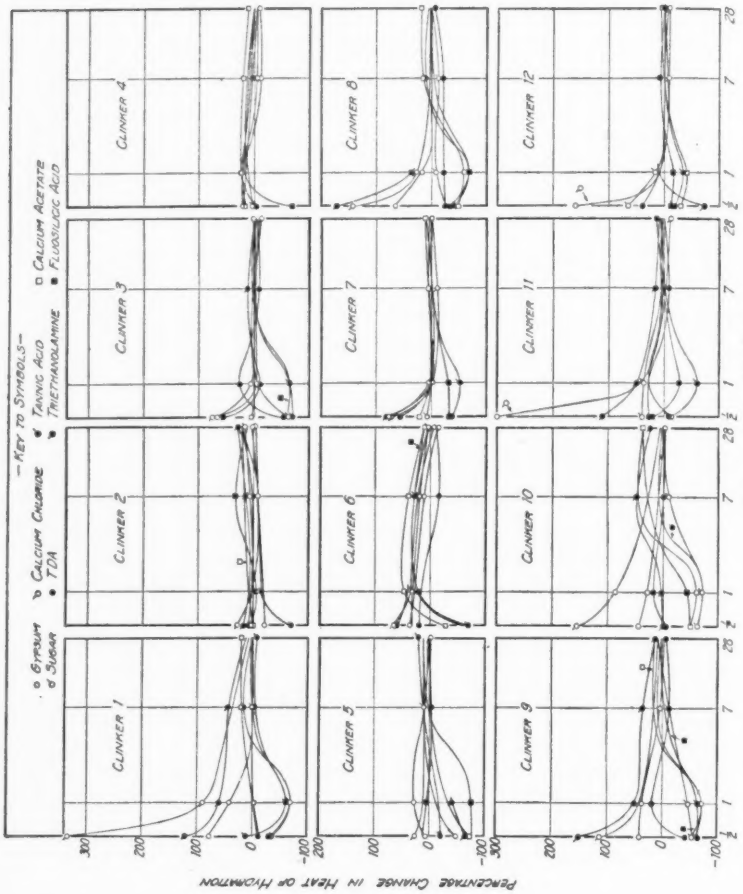

FIGURE 3.—*Effects of addition agents on the heats of hydration of clinker pastes.*

3. STRENGTHS

The results of the strength tests are presented in table 8. Because the 2½-hr pastes were frequently rather stiff, many of the specimens could not be fabricated properly. For this reason the strengths of the ½-hr pastes are the more reliable. The strengths of the specimens made from the ½-hr pastes were calculated as percentages of the strengths of the test pieces containing no added material and are presented in table 8. Few of the pastes containing triethanolamine were workable, and the strengths of specimens containing it are omitted from table 8 and from the discussion.

It should be pointed out that the strength specimens were fabricated from pastes from which part of the added substance had been removed by filtration. Therefore, the amount originally added was not that present during the hardening of the specimens. However, the analyses of the extracted liquids, together with their volumes compared with the amount of water originally added [1], indicated that a large part of the addition remained in the paste.

TABLE 8.—*Strengths of specimens fabricated from filtered [a] pastes with and without additions*

Clinker	Age	Actual tensile strength; no addition	Relative tensile strength [b]							Actual compressive strength; no addition		Relative compressive strength [b]											
			Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Calcium acetate	Fluosilicic acid			Gypsum		Sugar		Calcium chloride		TDA		Tannic acid		Calcium acetate		Fluosilicic acid	
										Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar
	Days	*lb/in²*	%	%	%	%	%	%	%	*lb/in²*	*lb/in²*	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	1	0	(45) [c]	(0)	(90)	(0)	(0)	(40)	(0)	40	80	600	360	0	0	700	950	80	50	0	0	330	150	0	0
	3	110	150	50	240	100	50	220	60	470	900	180	150	50	50	240	270	100	80	90	70	230	260	50	40
	7	255	120	90	130	90	80	130	100	1,340	2,380	110	100	80	90	130	170	110	90	100	90	150	170	90	100
	28	375	110	110	110	100	100	110	110	2,720	4,520	90	90	100	110	110	120	90	90	100	100	140	150	110	110
2	1	50	180	160	240	200	90	250	140	250	440	110	140	80	110	140	180	110	130	60	60	100	140	80	100
	3	170	120	120	120	120	90	110	130	640	1,220	120	150	120	160	120	150	120	140	110	110	120	160	130	160
	7	280	100	110	110	110	80	90	110	1,210	2,200	100	140	130	160	100	126	120	150	110	100	140	160	150	170
	28	355	140	120	120	130	110	110	110	2,800	4,200	90	140	120	160	90	120	110	140	110	100	120	140	140	150
3	1	125	160	0	230	110	0	120	0	460	880	150	140	0	0	250	270	90	90	30	20	50	100	0	0
	3	345	110	100	100	110	80	110	80	2,020	3,870	100	80	90	100	110	100	90	90	80	80	100	80	60	80
	7	440	110	100	100	100	90	100	90	3,150	6,000	100	90	90	100	100	90	110	100	100	90	100	90	90	100
	28	515	100	100	90	100	100	90	90	4,640	8,190	110	90	100	100	100	80	110	100	100	100	90	80	90	110
4	1	100	130	0	210	90	0	90	0	450	650	130	160	0	0	150	170	90	80	0	0	50	90	0	0
	3	230	120	120	150	70	110	130	100	1,440	1,690	100	160	90	130	110	140	90	80	80	120	100	210	50	110
	7	260	130	120	150	100	110	130	120	2,310	2,460	100	170	110	140	100	140	90	90	100	120	110	210	90	110
	28	345	120	110	120	110	110	130	120	3,610	3,410	100	170	100	140	90	120	100	110	110	110	110	190	100	110
5	1	70	210	0	250	80	0	60	0	170	500	280	190	0	0	360	220	170	70	0	0	80	30	0	0
	3	180	150	130	160	90	90	160	110	870	1,660	130	130	100	120	170	160	110	60	100	60	120	150	50	80
	7	285	120	110	140	80	80	120	90	1,760	2,550	110	120	110	140	120	150	110	80	110	90	110	190	90	90
	28	355	130	120	120	100	110	130	90	3,450	4,230	100	120	100	120	90	130	100	90	110	70	110	170	100	100
6	1	75	250	0	250	70	0	260	0	300	490	220	270	0	0	240	280	100	80	0	0	160	210	0	0
	3	155	190	160	190	80	130	210	140	1,210	1,330	120	200	100	160	150	250	70	80	100	110	140	310	75	140
	7	255	160	130	160	70	100	180	120	2,130	2,260	100	170	120	160	120	190	80	80	120	130	150	290	130	150
	28	380	130	110	120	90	100	120	110	3,460	3,810	120	150	120	140	100	150	80	90	120	100	130	220	130	120
7	1	35	490	0	630	70	0	50	0	230	410	250	260	0	0	290	350	40	60	0	0	40	60	0	0
	3	200	150	100	150	110	80	90	80	1,150	1,380	120	190	80	130	130	200	80	130	60	70	110	130	20	80
	7	250	140	70	140	120	90	100	90	2,240	2,370	110	160	90	110	100	180	90	140	80	80	100	120	60	80
	28	235	180	130	190	180	120	140	130	3,810	2,990	110	200	90	110	90	180	90	160	80	90	80	120	80	90
8	1	30	320	0	630	0	0	0	0	100	240	420	250	0	0	550	480	0	0	0	0	0	0	0	0
	3	170	110	100	160	90	100	140	60	630	1,350	160	130	70	110	210	190	130	80	100	90	170	150	10	40
	7	260	100	110	140	80	110	120	120	1,490	2,420	100	110	100	130	140	160	110	70	110	110	120	130	90	110
	28	360	120	110	120	100	110	130	120	2,900	4,490	110	110	110	130	110	120	110	90	120	110	130	150	120	120

See footnotes at end of table.

TABLE 8.—*Strengths of specimens fabricated from filtered[a] pastes with and without additions*—Continued

Clinker	Age	Actual tensile strength; no addition	Relative tensile strength[b]							Actual compressive strength; no addition		Relative compressive strength[b]									
			Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Calcium acetate	Fluosilicic acid			Gypsum		Sugar		Calcium chloride		TDA		Tannic acid		Calcium acetate		Fluosilicic acid	
										Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar
	Days	*lb/in*	%	%	%	%	%	%	%	*lb/in*	*lb/in*	%	%	%	%	%	%	%	%	%	%	%	%	%	%
9	1	40	350	0	450	0	0	0	0	150	260	390	310	0	0	410	450	0	0	0	0	0	0	0	0
	3	220	130	0	140	70	50	100	50	1,020	1,600	150	140	0	0	160	180	90	60	60	50	80	120	40	50
	7	290	130	100	130	80	100	110	110	1,970	2,740	100	110	90	110	120	150	80	70	90	110	110	160	80	100
	28	440	100	80	100	80	90	100	90	3,500	4,510	100	100	100	140	100	120	80	80	100	110	100	140	100	120
10	1	0	(85)	(0)	(125)	(40)	(0)	(0)	(0)	0	0	(390)	(400)	(0)	(0)	(440)	(780)	(140)	(110)	(0)	(0)	(0)	(0)	(0)	(0)
	3	140	110	30	170	80	40	100	100	690	860	120	120	60	30	150	220	80	70	60	60	100	110	80	100
	7	195	120	100	170	80	90	130	130	1,140	1,520	110	120	100	110	130	190	100	80	90	110	120	170	110	130
	28	365	110	100	120	90	100	120	100	2,340	3,180	100	110	110	130	100	140	100	80	100	110	140	180	120	140
11	1	60	230	0	410	50	0	0	0	130	260	370	350	0	0	650	550	100	90	0	0	0	0	0	0
	3	220	130	110	160	100	70	130	50	1,010	1,440	150	170	90	150	180	220	100	110	80	90	130	160	10	50
	7	300	140	110	130	100	100	110	100	2,250	2,610	120	170	100	150	120	150	90	120	100	120	110	150	80	90
	28	380	120	120	120	110	90	110	100	3,820	3,310	120	210	110	170	110	170	100	180	110	140	100	160	100	140
12	1	0	(185)	(0)	(230)	(70)	(0)	(0)	(0)	0	0	(510)	(1,230)	(0)	(0)	(730)	(1,630)	(80)	(290)	(0)	(0)	(0)	(0)	(0)	(0)
	3	250	130	90	130	90	40	100	70	750	1,630	180	190	110	100	240	190	120	130	90	50	150	100	50	40
	7	260	160	100	140	120	90	110	90	1,470	2,160	160	190	120	110	160	180	130	160	110	80	140	130	110	90
	28	355	140	100	130	120	80	110	80	2,670	3,090	150	220	120	100	140	170	120	160	120	80	130	150	120	100

[a] At 7 minutes.
[b] These strengths are expressed as percentages of the strengths of the similar specimens without addition.
[c] Figures in parentheses are the actual strengths in pounds per square inch.

It is considered that variations of the strengths between 90 and 110 percent should be classified as not significant. A close examination of table 8 will show exceptions, but in general the effects of the added materials were as follows:

Gypsum and calcium chloride increased nearly all the strengths, both tensile and compressive, sometimes by several hundred percent at the early ages. The increases caused by calcium chloride were usually larger than those caused by gypsum.

Sugar reduced nearly all the 1-day strengths to zero. Clinker 2 was an exception. At 3 days, clinker 9 developed no strength, but only a few of the other clinkers showed a reduction and several showed an increase. At 7 and 28 days many of the strengths were increased. Notwithstanding the fact that sugar is generally considered harmful, it is apparent that in the amounts added in these tests, it did not reduce the strengths developed by the clinker pastes after the first few days.

TDA (together with the water in which it was dissolved, 0.23 percent by weight of the clinker) reduced to zero the 1-day strengths of two of the clinkers. A few of the strengths at 1 day were increased, but the majority were either unchanged or reduced by TDA. At 7 and 28 days the tendency of TDA was, with a few exceptions, to change the strengths by only small amounts.

Tannic acid reduced nearly all the 1-day strengths to zero. At 3 days many of the strengths were decreased and only a few were increased. At 7 and 28 days in the majority of cases, tannic acid had little effect on the strengths.

Calcium acetate reduced the 1-day strengths of a majority of the clinkers. In five cases the strengths were reduced to zero. However, in a few cases rather large increases in the 1-day strengths were caused by calcium acetate. At the later ages, calcium acetate increased the strengths of a majority of the clinker pastes.

Fluosilicic acid reduced nearly all the 1-day strengths to zero. Here again clinker 2 was an exception. At 3 days the majority of the strengths were reduced, but at 7 and 28 days the strengths were left unchanged or slightly increased by fluosilicic acid.

4. SUGAR SOLUBILITY AND FLOC TESTS

The results of the sugar-solubility test are reported in table 9. Although the Merriman test was designed for use with cements, i.e., clinker plus gypsum, it may be of interest to consider the effects of the additions on the clinkers in terms of the ability of the material to pass the sugar-solubility test. The highest permissible "clear point" a cement may show and pass the test is 10 ml of 0.5 *N* HCl. It will be seen that only three clinkers are below this limit. Gypsum lowered all the clear points sufficiently for three clinkers having high clear points to be included in the group below 10 ml of 0.5 *N* HCl. Calcium chloride increased the clear points of many of the clinkers, whereas TDA affected them only slightly. Tannic acid decreased nearly all the clear points by rather large amounts in some cases, and brought two clinkers having high clear points into the group having clear points of less than 10 ml of 0.5 *N* HCl. Triethanolamine increased most of the clear points but decreased a few, in one case sufficiently to include the clinker in the group passing the test for cement. Calcium acetate slightly increased the majority of

the clear points. Fluosilicic acid lowered all the clear points, sufficiently for six clinkers with high clear points to include them in the group having clear points of less than 10 ml of 0.5 *N* HCl. None of the materials caused the clear points of the three clinkers, No. 1, 5, and 9, to increase sufficiently to exclude them from the group passing the sugar-solubility test for cement.

TABLE 9.—*Results of Merriman sugar-solubility test on cement clinkers with and without added materials*

Clinker	[a] Filtrate	Volume of 0.5 *N* hydrochloric acid used in titration							
		No addition	Gypsum	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
		ml	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
1	Ep	2.1	2.0	1.6	1.9	1.9	2.1	1.9	1.6
	Cp	2.1	2.0	1.6	1.9	1.9	2.1	1.9	1.6
2	Ep	31	27	28	35	44	37	35	30
	Cp	40	32	37	46	58	45	44	39
3	Ep	43	38	44	42	39	45	46	4.0
	Cp	61	50	63	60	55	63	63	4.0
4	Ep	27	3.2	33	27	2.3	2.4	27	2.1
	Cp	37	3.2	46	38	2.3	2.4	38	2.1
5	Ep	2.3	2.4	2.3	2.6	1.9	2.4	2.0	1.7
	Cp	2.3	2.4	2.3	2.6	1.9	2.4	2.0	1.7
6	Ep	25	7.7	29	25	13	22	26	2.7
	Cp	36	8.7	44	36	19	32	38	2.7
7	Ep	41	34	43	42	43	42	43	31
	Cp	63	49	66	65	67	66	66	55
8	Ep	22	10.1	29	26	6.8	24	29	2.3
	Cp	33	12.4	42	38	8.2	36	43	2.7
9	Ep	2.6	2.5	2.7	2.6	2.3	2.8	2.6	1.7
	Cp	2.6	2.5	2.7	2.6	2.3	2.8	2.6	1.7
10	Ep	19	7.3	21	22	15	22	24	5.5
	Cp	25	11.3	26	26	19	30	32	7.8
11	Ep	32	7.5	38	33	24	30	34	1.8
	Cp	39	8.4	57	39	38	46	51	1.8
12	Ep	49	45	52	49	47	48	49	30
	Cp	72	65	74	71	70	70	72	47

[a] Ep, end point; Cp, clear point.

The weights of the ignited precipitates obtained in the floc tests are given in table 10 as percentages of the total weights of clinker taken. In a few determinations, part of the hardened clinker sloughed off during filtration and was included in the weight of the floc. This accounts for the high values obtained in a number of cases. In general, the added materials affected the results of the floc test only slightly.

TABLE 10.—*Results of Paul floc test of cement clinkers with and without added materials*

[Floc in percent by weight of clinker. All observed quantities of floc were "none" except for gypsum with clinkers 3, 4, 6, and 12, which were "small", and clinkers 7 and 11, which were "medium"]

Clinker	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	%	%	%	%	%	%	%	%	%
1	0.1	0.5	0.1	0.2	0.2	0.8	0.3	0.3	0.1
2	.3	.3	.4	.7	.4	.2	.6	.4	.2
3	.1	.3	.1	.2	.3	[a] 1.0	.3	.3	.1
4	.1	.2	.2	.3	.2	0.3	.2	.2	.1
5	.2	.2	.2	.2	.2	.2	.2	.1	.1
6	.1	.5	.2	.2	.2	.3	.3	.2	.2
7	.2	2.4	[a] 10.6	.5	.7	[a] 7.6	.9	[a] 2.1	[a] 7.7
8	.3	0.3	0.3	.3	.3	0.3	.3	0.2	0.3
9	.3	.3	.3	.3	.3	.3	.3	.3	.2
10	.2	.2	.2	.2	.2	.2	.2	.2	.2
11	.2	1.3	.3	.3	.3	[a] 4.8	.3	.2	[a] 3.0
12	.4	0.7	.4	.4	.3	[a] 4.7	.3	.3	0.5

[a] Particles of clinker included in weight of floc.

V. SUMMARY

The effects of added materials on 12 commercial portland cement clinkers were studied by comparing the results of tests of clinker samples containing the various additions with the results of identical tests of the clinkers alone. Determinations were made of (1) the temperature changes of the clinker pastes during one or more days after mixing, (2) the heats of hydration of the clinkers, (3) the tensile and compressive strengths of mortars and the compressive strengths of concretes, (4) the consistencies of concretes, (5) the sugar solubilities of the clinkers according to Merriman's method, and (6) the amounts of floc developed by the clinkers according to Paul's test. The materials added were gypsum, sugar (sucrose), calcium chloride, TDA, tannic acid, triethanolamine, calcium acetate, and fluosilicic acid.

It was found, in general, that while the added materials sometimes caused marked changes in the behavior of the clinker pastes during their early history, these changes were practically negligible at 28 days.

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SOME PROPERTIES OF HEAT-SETTING REFRACTORY MORTARS

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ABSTRACT

Twelve brands of the heat-setting type of refractory mortar were studied with respect to sieve analysis, pyrometric cone equivalent, amount of mixing water required, troweling and drying properties, and strengths after heating at various temperatures. The tendency of the mortars to shrink, crack, and adhere when exposed to high temperatures, both in fusion blocks and in units of three bricks each, was also investigated.

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I. INTRODUCTION

There are four materials ordinarily used for bonding fire-clay bricks or refractory shapes. Ground plastic fire clay was the generally accepted medium for many years, but with the improvement in refractories, the heat-setting mortar and the wet and dry types of air-setting mortars were developed and marketed. Federal specifications based on the results of investigations made at the National Bureau of Standards have already been prepared for fire clay and the two types of air-setting mortars. It is planned that the data reported in the present paper will be used for a similar purpose in the case of the heat-setting type of mortar.

II. MATERIALS

Twelve refractory mortars of the heat-setting type were supplied by eight manufacturers. One of these mortars was originally submitted as an air-setting mortar of the dry type, but because it had very little strength after air-setting, it was considered a heat-setting mortar.

III. PREPARATION OF SPECIMENS AND METHODS OF TESTING

1. MORTARS

Each mortar was mechanically mixed with water for 1 hour, during which period the water content was adjusted to obtain the proper consistency for troweling as judged by "feel." After soaking the mortars overnight they were mixed for an additional 4 hours before testing them. All the tests were made on mortars so treated except the sieve analysis test,[1] which was made after the 1-hour mixing. The amount of mixing water was determined by drying samples of approximately 200 g to a constant weight at about 105° C. The pyrometric cone equivalents were determined according to the ASTM standard method.[2] The flow-table test was made as described in Federal Specification SS–C–158,[3] and also in the ASTM standard specifications.[4]

The troweling tests were made with the machine described by Heindl and Pendergast.[5] A ¼-in. layer of mortar was spread evenly by hand-troweling on the upper 9- by 4½-in. face of a brick by means of a template. Using such specimens, two tests of troweling properties were made by reducing this ¼-in. layer to ⅛ in. in 1 stroke, and to ⅛ in. in 25 strokes (0.005 in. per stroke), respectively. The mortar caps were examined before drying for uniformity of thickness and adherence to the brick and, after drying, for cracks.

The modulus of rupture (transverse strength) was determined on mortar bars 6 by 1 by ¼ in. after drying for 27 hours at approximately 105° C. The bars were placed on supports 5 in. apart and loaded midspan. For convenience in reporting the results of the breaking tests, reference hereafter to the "original" position indicates that the surfaces of the bar in the test machine were in the same position as they were when made, that is, the same surface was uppermost on both occasions. Conversely, reference to "inverted" position indicates the surfaces were in reverse position during the tests. Half of the 10 mortar bars were tested in the original position in the cross-breaking machine and the other half in the inverted position.

The linear shrinkage determinations were made on three bar specimens of each mortar after each of three heat treatments, namely at 105°, 1,350°, and 1,500° C, respectively.

Tests of the mortars for adherence and also observations for shrinkage were made by heating each mortar in a fusion block having a compartment ½ in. deep. The heat treatments were identical with those used for the bar specimens.

2. MORTAR AND BRICK

Assemblies of two half-brick and mortar were used for determining the strength of brick-to-mortar bond. The brick were cut parallel to the 2½- by 4½-in. faces into two equal parts. A laboratory screw

[1] In general, the test was similar to that described in Standard Method of Test for Particle Size of Ground Refractory Materials, ASTM Designation C 92–36, Am. Soc. Testing Materials Standards, pt. 2, Nonmetallic Materials—Constructional, p. 195 (1939).

[2] Pyrometric Cone Equivalents of Refractory Materials, ASTM Designation C 24–35, Am. Soc. Testing Materials Standards, pt. 2, Nonmetallic Materials—Constructional, p. 214 (1939).

[3] Cements, Hydraulic, General Specification.

[4] Standard Specifications for Masonry Cement, ASTM Designation C 91–40, Am. Soc. Testing Materials Standards, Supplement, pt. 2, p. 1–7 (1940).

[5] J. Research NBS **23**, 7 (1939) RP1219.

press [6] was used in bonding the two half-brick with mortar. Sections of ⅛-in. drill rod were used as temporary spacers to obtain uniform thickness of mortar joints. The modulus of rupture of the mortar joint was determined after drying the specimen for 27 hours at about 105° C. The specimens were placed on supports 8 in. apart and loaded midspan.

A second type of brick-and-mortar assembly was made, consisting of a pier of two standard-sized brick and two half-brick laid flat to give one vertical joint between the two horizontal joints. Three of these piers were laid up with a troweled joint ⅛ in. thick. The piers dried at 105° C and also heated at 1,350° and 1,500° C, were examined, when cool, for defects of the mortar cap and mortar joints.

The bonding ability of a mortar may be judged by grasping the top brick in a pier made of three brick as described above, and lifting it. If the mortar and brick pier remains intact, it can be assumed that the mortar has reasonably good bonding properties. This simple test was made on piers heated for 1 hour at 1,350° and at 1,500° C and cooled.

IV. RESULTS AND DISCUSSION

1. MORTARS

(a) SIEVE ANALYSIS

The results of the sieve analysis are given in table 1, columns 2 to 7. Less than 1 percent was retained on the No. 20 sieve for 8 of the 12 mortars. In the case of five of the mortars, over 60 percent passed the No. 200 sieve. Mortars *P1* and *Y1*, on the other hand, had the largest percentage of coarse fractions, only 35 percent having passed the No. 200 sieve.

(b) PYROMETRIC CONE EQUIVALENT

The pyrometric cone equivalent of the mortars, listed in table 1, column 8, ranged from 27–28 to 35–36. The refractoriness of the mortars was fairly high, since the pyrometric cone equivalent was above 30 in all but one instance.

(c) MIXING WATER AND FLOW-TABLE TEST

The amounts of water, in terms of percentage of the dry weight of the mortar, used for bringing the mixtures to the proper consistencies for troweling are given in table 1, column 9. The amount of water ranged from 21.2 to 41.5 percent. In general, the mortars which contained greater proportions of coarse particles, as indicated by the total percentage retained on the No. 200 sieve, required the least amounts of water for tempering. The two exceptions to this relation are mortars *N1* and *O1*, which contained the lesser proportions of coarse particles. Both of these mortars showed definite alkaline reaction when tested with 0.2 *N* hydrochloric acid and the deflocculation resulting from this alkalinity no doubt accounted for the low percentages of water required. The other two mortars which gave indications of alkalinity were *P1* and *R1*. Both contained high percentages of coarse-grained material, in fact, *P1* led all others in that respect, and hence any deflocculating action which could have been caused by the alkalies present may have been largely nullified.

[6] J. Research NBS **23**, 7 (1939) RP1219.

TABLE 1.—*Some properties of heat-setting refractory mortars*

Mortar	Sieve analysis [1]						Pyrometric cone equivalent	Water content of neat mortar	Flow-table readings	Troweling properties. Spreading and reducing layer—		Drying properties of troweled caps	
	Retained on No. 20	Passed No. 20, Retained on No. 40	Passed No. 40, Retained on No. 60	Passed No. 60, Retained on No. 100	Passed No. 100, Retained on No. 200	Cumulative total not passing No. 200				From ¼ in. to ⅜ in. in 1 stroke	From ¼ in. to ⅜ in. in 25 strokes	Adhered	Cracked
1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Percent	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Cone*	*Percent*	*Percent*			*Percent*	
J 1	0.0	1.7	16.2	21.0	17.2	56.1	31	25.6	72	Good	Good	100	No.
K 1	.2	1.8	9.3	12.9	14.0	37.2	30–31	36.0	76	do	do	0	Do.
N 1	.0	0.2	4.4	9.9	14.5	29.0	32–33	22.8	82	do	do	95	Do.
O 1	.0	.1	3.3	10.6	15.2	29.2	31–32	25.7	70	do	Poor	35	Do.
P 1	.2	12.2	20.2	16.3	15.7	64.6	31	26.4	75	Fair	Fair	100	Do.
Q 1	.1	0.9	17.2	20.1	19.1	57.4	31–32	32.0	65	Good	Good	100	Do.
R 1	1.9	12.7	21.4	12.1	11.2	59.3	35–36	24.6	77	do	do	95	Do.
S 1	0.1	6.5	20.9	16.1	12.9	56.5	35	22.2	74	do	do	100	Do.
T 1	1.2	8.7	9.0	9.5	9.6	38.0	32	41.5	79	do	Fair	0	Moderately.
U 1	1.5	11.5	9.8	7.7	7.7	38.2	31–32	39.0	57	do	Good	0	Do.
V 1	0.1	2.0	16.5	20.7	15.1	54.4	32	32.2	66	do	do	95	No.
Y 1	2.7	32.1	19.2	5.2	6.5	65.7	27–28	21.2	82	do	do	95	Do.

[1] U. S. Standard Sieve Series.

The results of the flow-table test of the mortars in a troweling consistency are given in table 1, column 10. The values range from 57 to 82, all but three being between 70 and 82, indicating that the initial consistency of most of the mortars was very nearly the same.

(d) TROWELING

The results of the mechanical-troweling tests are given in table 1, columns 11 and 12. These tests gave an indication of the workability of the mortars. In the one-stroke test all mortars except *P1*, which lacked sufficient plasticity, proved satisfactory, but in the 25-stroke test mortars *O1*, *P1*, and *T1* were the exceptions. Mortar *O1* was rated "poor" because of excessive stickiness, resulting in its adhering to the trowel and being partially pulled from the brick.

The condition of the mortar caps on the brick, after troweling and drying, are given in table 1, columns 13 and 14. Mortars *K1*, *T1*, and *U1* showed no indication of adherence to the brick, and mortar *O1* adhered only about one-third. The remainder had good adherence. The degree of adherence of the mortar cap, however, was no indication of the bonding property of the mortar when used in joints. The caps were remarkably free from drying cracks; only 2 (*T1* and *U1*) of the 12 showed any development of cracks and these were not serious.

In table 2 are given the average transverse strengths of the neat-mortar bars after heating them at 105°, 1,350°, and 1,500° C. In each case three values are given: (1) the average for not less than five bars broken in the inverted position, (2) a similar average for bars broken in the original position, and (3) the averages for both positions. The results obtained after heating the bars at 105° C indicate no significant difference in strength with position of specimen during loading. However, the specimens, after heating at 1,350° and 1,500° C, showed strengths averaging about 18 percent greater when tested in the inverted position than when tested in the original position. This relation is the reverse of the findings in tests of air-setting mortars [7] of the wet and dry types.

The average transverse strength of the neat mortars dried at 105° C ranged from 0 to 290 lb/in^2, those heated at 1,350° C from 350 to 4,720 lb/in^2, and those heated at 1,500° C from 1,705 to 5,550 lb/in^2, all the specimens being cooled to room temperature before testing.

The linear shrinkages of neat mortars resulting from heating at 105°, 1,350°, and 1,500° C and cooling are given in table 2. The two mortars, *T1* and *U1*, which show the highest shrinkages after heating at 105° C, were the only ones which cracked on drying after the troweling tests.

2. MORTAR AND BRICK

The results of the transverse-strength tests made on assemblies of the two half-brick bonded with mortar are given in table 2. After heating at 1,350° C, eight of the 12 mortars indicated no significant bonding of the end faces of half-brick, as indicated by lack of cross-breaking strength of the brick-and-mortar units. After heating at 1,500° C, however, all but four of the mortars had good adherence or bonding properties, the strengths of the assemblies ranging as

[7] R. A. Heindl and W. L. Pendergast, *Properties of air-setting refractory bonding mortars of the wet type*, J. Research NBS **23**, 7 (1939) RP1219; *Some properties of dry air-setting type of refractory bonding mortar*, **28**, 401 (1942) RP1461.

TABLE 2.—*Strength and shrinkage of heat-setting mortars after heating at several temperatures*

Mortar	Transverse strength [1] (modulus of rupture) of neat-mortar bars after heating at—			Linear shrinkage [2] of neat-mortar bars after heating at—			Transverse strength (modulus of rupture) of two-half-brick-and-mortar assemblage after heating at—	
	105° C	1,350° C	1,500 C°	105° C	1,350° C	1,500° C	1,350° C	1,500° C
	lb/in.²	*lb/in.²*	*lb/in.²*	*Percent*	*Percent*	*Percent*	*lb/in.²*	*lb/in.²*
J1	230 240 235	1,590 1,570 1,580	2,765 2,365 2,565	2.4	1.7	3.0	90	520
K1	210 200 205	5,200 4,235 4,720	3,010 2,950 2,980	6.9	5.9	4.4	0	0
N1	125 135 130	3,885 2,625 3,220	6,020 5,090 5,550	4.8	3.5	6.3	0	0
O1	160 150 155	4,170 3,490 3,785	4,750 4,330 4,540	6.3	4.1	6.4	0	0
P1	165 175 170	2,120 2,035 2,080	3,040 2,480 2,760	2.5	2.9	5.3	25	300
Q1	160 150 155	2,680 2,355 2,515	4,120 2,680 3,400	6.2	3.1	5.6	0	365
R1	0	1,205 895 1,050	2,315 2,180 2,150	0.9	0.8	1.5	180	665
S1	190 180 185	1,635 1,780 1,710	2,990 2,175 2,580	2.5	1.4	3.1	0	[3] 260
T1	170 180 175	2,405 2,405 2,405	3,115 2,730 2,920	9.2	3.7	5.1	0	0
U1	300 290 290	3,405 2,920 3,160	3,255 2,750 3,005	7.7	6.4	7.4	0	145
V1	110 95 105	2,075 2,060 2,070	3,140 4,530 3,835	6.5	3.2	4.8	0	[3] 85
Y1	190 205 195	350 345 350	1,755 1,655 1,705	4.0	1.0	3.9	95	460

[1] The 3 values determined for each mortar after having been heated at each of 3 temperatures represent, in the order given, the averages for: (1) 5 specimens broken with the surface that was originally at the top during drying in tension ("inverted position"), (2) 5 specimens with the surface that was originally on the bottom in tension ("original position"), (3) all specimens.

[2] Values tabulated in columns for 1,350° and 1,500° C are burning shrinkages.

[3] Average of 2 specimens.

high as 665 lb/in². In all cases the lack of strength in the assembly was due to failure of bonding of the mortar and brick and not due to weakness of the mortar.

The results of the visual examination of the mortars in the joints of the three-brick piers and in the fusion blocks after heating at 105°, 1,350°, and 1,500° C are given in table 3. Only those cracks described as "bad" would be considered as affecting the quality of the mortar. Almost without exception the information relative to the shrinkage and cracking of a mortar, whether obtained from examination of a fusion block or of a cap, correlated with that obtained on the joints. The following exceptions may be cited. (1) The shrinkage of *K1* was less in the joints than in the fusion block or in the cap, (2) the shrinkage of *O1* in the joints and in the fusion block was less than in the cap with comparable heat treatment and, (3) the appearance of mortar *Q1* in the joints of the pier and that in the fusion block heated at 1,500° C did not correlate.

TABLE 3.—*Appearance of mortar in fusion block, cap and in joints of three-brick-and mortar assemblage*

Mortar	Appearance of mortar in ⅛-in. joints [1] of pier after heating at—			Appearance of mortar in fusion block after heating at—			Condition [2] of ⅛-in. cap of mortar after heating at—		Bond in pier satisfactory after heating for 1 hour at—	
	105° C	1,350° C	1,500° C	105° C	1,350° C	1,500° C	105° C	1,350° C	1,350° C	1,500° C
J1	Good	⊥ and ∥ cracks.	Good	Slight shrinkage	Slight to moderate shrinkage.	Slight shrinkage. No adherence.	Good	Good	Yes	Yes.
K1	⊥ and ∥ cracks.	Moderate ⊥ and ∥ cracks.	Moderate ⊥ and ∥ cracks.	Moderate shrinkage.	High shrinkage. No adherence.	High shrinkage. No adherence.	Badly cracked. 75% not bonded.	Badly cracked. 80% not bonded.	No	Do.
N1	do	do	do	Slight shrinkage	Moderate shrinkage	Moderate shrinkage	Slightly cracked	Slightly cracked	do	No.
O1	Moderate ⊥ and ∥ cracks.	do	Bad ⊥ and moderate ∥ cracks.	do	do	do	Badly cracked	Badly cracked. 25% not bonded.	Yes	Yes.
P1	Good	Good	Good	Good	Good	Good	Good	Good	do	Do.
Q1	do	do	Bad ⊥ and slight ∥ cracks.	Slight shrinkage	Slight shrinkage	Slight to moderate shrinkage.	do	Slightly cracked. 10% not bonded.	do	Do.
R1	do	⊥ and ∥ cracks.	Thermal cracks. Fused.	do	do	do	do	Slightly cracked	do	Do.
S1	do	Good	Good	do	Slight to moderate shrinkage.	Slight to moderate shrinkage.	do	Good	do	Do.
T1	Moderate ⊥ and ∥ cracks.	Bad ⊥ and ∥ cracks.	Bad ⊥ and moderate ∥ cracks.	Moderate shrinkage.	High shrinkage. No adherence.	High shrinkage. No adherence.	Badly cracked. 50% not bonded.	Badly cracked. 80% not bonded.	do	Do.
U1	do	do	do	do	do	do	do	do	do	Do.
V1	Good	⊥ and ∥ cracks.	⊥ and ∥ cracks	Slight shrinkage	Moderate shrinkage	Moderate shrinkage	Good	Slightly cracked	do	Do.
Y1	do	Good	Good	do	Good	Slight shrinkage	do	Slightly cracked. 50% not bonded.	do	Do.

[1] Cracks occurring in the horizontal joints are designated ∥; those in the vertical joints ⊥.
[2] No reference to "adherence" indicates that bonding had taken place between mortar and fusion block.

In general, the cracking which occurred in the mortar joints and caps could have been predicted on the basis of selecting from the mortars listed in table 2, those having the highest shrinkage values after drying at 105° C.

The results of the test for judging the bonding ability of the mortars by grasping the top brick of a pier of three bricks bonded with mortar are listed in the last two columns of table 3. All the mortars proved satisfactory in the tests except *K1* and *N1*. Mortar *K1* failed in this test after having been heated at 1,350° C, and mortar *N1* failed both after heating at 1,350° and at 1,500° C.

V. SUMMARY

Twelve refractory mortars of the heat-setting type supplied by eight manufacturers were investigated.

The mortars were finely ground, as supplied, only one contained as much as 2 percent of material that would not pass a United States Standard Sieve No. 20. The refractoriness of the mortars, as indicated by the pyrometric cone equivalent, was high, all but one being above cone 30. The amount of mixing water ranged from 21.2 to 41.5 percent. The consistencies of the mortars, however, as indicated by the flow-table test, were, with three exceptions, within a narrow range. The ease of troweling on brick, determined mechanically, was considered satisfactory except for one mortar. After troweling and drying, three mortars failed to adhere to the brick, but cracking was absent in all but two cases and these were not serious. These two mortars also had the greatest drying shrinkages.

The average modulus of rupture of the neat mortars dried at 105° C ranged from 0 to 290 lb/in.^{2}; of those heated at 1,350° C, from 350 to 4,720 lb/in.^{2}; and of those heated at 1,500° C, from 1,705 to 5,550 lb/in^2. In the transverse tests the bonding strength of the mortars in assemblies of two half-brick and mortar, heated at 1,350° C and cooled, was poor, as indicated by the lack of any significant stregnth of 8 of the 12 mortars. Satisfactory bonding strength was shown, however, by 8 of the 12 mortars after the heat treatment at 1,500° C. On the other hand, when the mortars were tested for their bonding property by grasping the upper brick in a pier made up of three brick and motar and lifting it, the results were very different. In these tests only two mortars were observed to fail when heated at 1,350° C, and but one when heated at 1,500° C and cooled.

The majority of mortars included in this study would be considered of satisfactory quality with respect to the technical requirements in a Federal specification based on the results of this investigation.

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SOURCES OF ERROR IN PRECISE COMMERCIAL REFRACTOMETRY

By Leroy W. Tilton

ABSTRACT

Exclusive of compensators, the mechanical requirements for accurate refractometry to a few units of the fifth decimal place in index are difficult but not impracticable. Optical requirements are high because the symmetrical use of all apertures is, in general, not possible. If it is necessary to distinguish between index of sample referred to air at t or at t_0, this usually can be done by choice of a relative or an absolute temperature coefficient when correcting for temperature of the refractometer block. For an error of 1×10^{-5} in index of solids, the permissible prism of contact liquid is one-third fringe per centimeter as viewed in the exit pupil of the telescope. The requirements for minimum shielding of critically refracted rays, for absence of certain interference fringes in the field of view, and for surfacing of the illuminating prism are so related with reference to measurements on small samples of liquid that compromises are necessary in the design of precision refractometers.

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I. INTRODUCTION

Critical-angle methods of refractometry offer interesting possibilities of obtaining great sensitivity over a limited range in refractive index on specially designed instruments with carefully determined constants, as is shown by discussions such as those of Guild,[1] Simeon,[2] Smith,[3] Schultz,[4] and Straat and Forrest.[5] Various types of refractometers have been in use for many years in connection with the routine and control analysis of a wide variety of products. Specialized instruments have been developed for the more or less direct

[1] J. Guild, Proc. Phys. Soc. (London) **30**, 157–189 (1918) or Nat. Phys. Lab., Collected Researches **14**, 273–296 (1920).
[2] Frederick Simeon, Proc. Phys. Soc. (London) **30**, 190–203 (1918).
[3] T. Smith, Nat. Phys. Lab., Collected Researches **14**, 297–300 (1920).
[4] H. Schultz, Z. tech. Physik **3**, 90–93 (1922); Z. Instrumentenk. **48**, 26–30 (1928).
[5] H. W. Straat and J. W. Forrest, J. Opt. Soc. Am. **29**, 240–247 (1939).

determinations of such specific substances as sugar, butter, milk, and oils. Such instruments include both the Abbe and the dipping types, but the Abbe type with water-jacketed prisms predominates. This instrument has been more or less standardized and is the most commonly used instrument for measuring refractive indices of liquids and solids.

All these instruments have achromatizers that permit the use of a white-light source, and in this respect they differ from the Pulfrich refractometer,[6] which is much used in the optical-glass industry. The Pulfrich is designed for use with a spectral-line source and is somewhat more suitable for work on solid media than on liquid samples. Formerly it was customary to use Pulfrich or dipping refractometers whenever precise refractive indices were desired, but as a result of the greater convenience of the Abbe type with double prisms, the manufacturers have improved the design of these instruments and to some extent have simplified them so that they can now be used in precision measurements. The chief changes have been finer scale rulings, better bearings, and the omission of achromatizers in some instances. Certain details regarding the careful use of Abbe-type refractometers were recently discussed in another paper.[7] The high precision obtainable in using these instruments has prompted these further investigations of possible sources of inaccuracy.

II. INSTRUMENTAL AND OBSERVATIONAL ERRORS

It is difficult but not impracticable for a manufacturer to standardize and control his product within approximately the tolerances corresponding to ± 0.00005 in refractive index. This is demonstrated by the ability of some manufacturers to approximate these requirements in some instances, especially when concerned with precision refractometers. They have, as a rule, not attempted this high degree of standardization in making the usual type of Abbe refractometer, but even there such accuracy is sometimes approximated. Table 1 gives an idea of the optimum performance that is occasionally found for fourth-decimal-place Abbe refractometers. These examples are selected from numerous tests and represent the product of five manufacturers. In some cases, however, in order to get such good performance it was necessary to eliminate the maladjustment that results when the test slab that accompanies an instrument is incorrectly or inadequately marked. In all cases the scale settings were estimated to better than 0.1 division, and numerous settings and readings were averaged.

When in 1874 Ernst Abbe described the refractometer that now bears his name, he discussed [8] in a direct and simple manner the effects of erroneous constants adopted for a given instrument. Also the above-mentioned papers [9] by Guild, Simeon, Smith, Schultz, and Straat and Forrest cover, to some extent, the same subject. From Abbe's work, and from some of the other papers cited, it is evident that an error of ± 0.00005 in measurement of refractive index of the sample can be caused if the index of the glass block (refracting prism) of the refractometer differs from its supposed value by only ± 0.00006;

[6] A valuable paper by J. Guild on refractometers, with particular reference to the Pulfrich type, was published in 1918. See footnote 1.
[7] L. W. Tilton, J. Opt. Soc. Am. **32**, 371 (1942).
[8] See Gesammelte Abhandlungen von Ernst Abbe, **II**, 136 (Gustav Fischer, Jena, 1906).
[9] See footnotes 1 to 5, p. 311.

also if the refracting angle of the block is in error by about ±10 seconds.

TABLE 1.—*Correction data on exceptionally good Abbe refractometers of the usual type, with achromatizers, that permit readings, by estimation of tenths, to the fourth decimal place of index*

[The product of five manufacturers, including the domestic corporations Bausch & Lomb Optical Co., Industro-Scientific Co., and the Spencer Lens Co., is represented, but in each case the adjustment approximates the optimum and was made irrespective of the particular test plate that accompanied the instrument.]

Line of scale	[a] Required corrections ×10⁴				
	A	B	C	D	E
1.333	0	+6	+1	+1	+7
1.392				+8	
1.395	−3				
1.434	0			+9	
1.459	+2	−4		0	
1.461	+2		0		−6
1.479		−4			
1.480	+1				
1.490				−2	
1.504	−1	−1	−3	−8	
1.515				−8	
1.519	−1		−1		+4
1.522			−1		
1.569	−6	−4	0	−9	+3
1.612	+2	−1	−1	−2	+2
1.656	−4		+1		
1.672	−1	−1	+2	−8	−4

[a] Corrections for water, 1.333, are more often positive than negative because of the negative errors that are likely to be caused by shielding (section VI) or by fringes (section VII).

On a refractometer with an index range 1.3 to 1.7 and for an unfavorable case, a determination of the relative orientation of the telescope and the refracting prism must be accurate to within about ±15″, or for one with index range 1.3 to 1.5 a determination must be accurate to within about ±20″, in order that a resulting error in index of the sample shall not exceed ±0.00005. With reference to most instrumental matters, such as the bearings and the scale rulings of refractometers, the accuracy of orientation and its determination within 15 or 20″ presents no serious problem. For Abbe refractometers of the usual dimensions this accuracy of 15″ in the evaluation of prism orientation means that many lines of the scale must be correctly positioned along the arc within about 10 microns, and for an unfavorable case the axis of rotation of the prism must intersect the sector center within about 25 microns.

Pyramidal error of the Amici prisms in Abbe refractometers causes index readings to differ for a given sample, depending on which of two possible settings of the achromatizer is used. Because of the way in which the two Amici prisms are mounted and rotated, the combined components of the lateral deviations are, in the direction of the resultant dispersion, oppositely directed for the two achromatizing positions, as shown in figure 1, and the mean of the index readings is free from influence of the pyramidal error.

More insidious are the effects of deviations of sodium light by a compensator in the direction of the principal planes. See figure 2. Even in Abbe's time it was considered that critical workmanship could, with certainty, hold this deviation by an Amici prism to within 1′ of arc, and he pointed out the merit of combining prisms having deviations with opposing signs, so that the consequent error in

refractive index need never reach 2×10^{-4}. Control of deviation within 30″ is now considered practicable. Nevertheless, in the course of criticial studies on numerous refractometers, including instruments of foreign and of domestic manufacture, the writer sometimes finds instruments of the Abbe type that have a total compensator deviation variation appreciably in excess of 2×10^{-4}, and occasionally it is as high as 2×10^{-3}. In such cases the labor of a precise calibration of the instrument is excessive. Figure 3 shows approximate calibration

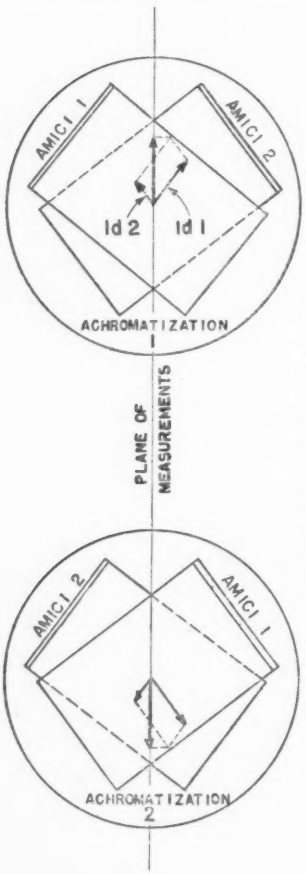

FIGURE 1.—*Effect of lateral deviation (ld) by Amici prisms.*

Mean readings taken after opposite settings of the compensator are free from effects of pyramidal error. See text of this paper; also L. W. Tilton, J. Opt. Soc. Am. **32**, p. 373-74 (1942).

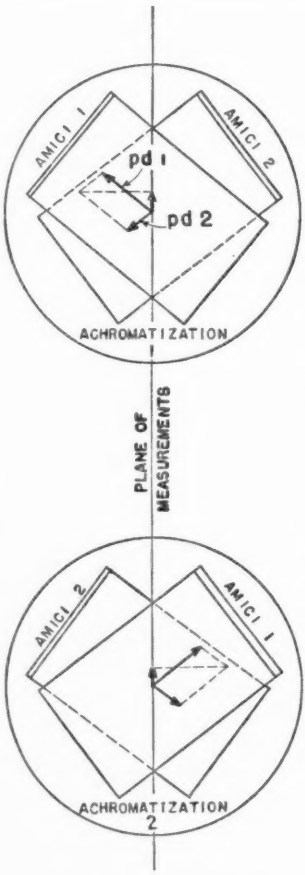

FIGURE 2.—*Effect of principal plane deviation (pd) by Amici prisms.*

Mean readings are free from compensator deviation only if the manufacturer has properly paired the Amici prisms, so that $pd\,1 = -pd\,2$.

curves for an instrument having excessive compensator deviation variation. These curves are averages for the two possible achromatizations that have approximately equal numerical drum readings.

The difficulty of making good compensators for critical-angle refractometers reading to the fifth decimal of index is an important reason for the present tendency to substitute monochromatic sources for white light. However, as a result of his experience with refractometers having specially built compensators, the writer believes that it is not necessary to abandon the use of a white-light source when measuring only *D*-lines index and seeking an accuracy of say ±0.00004 in

index. Practically, the cost of making compensators sufficiently accurate for the purpose may be excessive.

The only important observational errors, aside from maladjustment or failure to adjust the instrument to a proper reading for the test

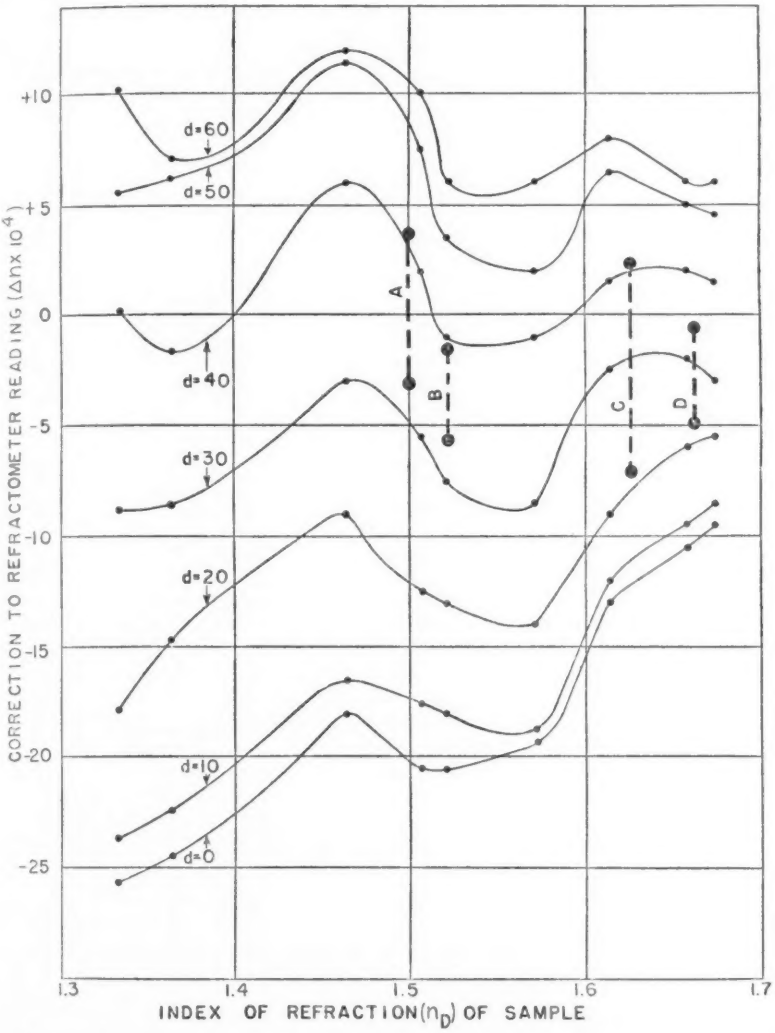

FIGURE 3.—*Calibration curves for refractometer having a defective compensator.*

The required corrections are functions of index and also of the compensator drum reading, *d*. The length of line *A* shows the difference in correction for benzene, which achromatized at a drum reading of 32, and for a sample of glass having exactly the same index, which, however, achromatized at 41. Similarly, lines *B*, *C*, and *D* show, respectively, the differences in correction for tung oil, carbon disulfide, and monobromnaphthaline, as compared to glasses of identical refractivity.

slab, are those committed in setting the refracting prism with respect to the telescope axis and in determining that angular relationship. Certainly the *precision* of setting cross hairs on the critical border is always ample if a reasonably sharp dividing line is obtainable. The

writer has found that such optical settings can be made with a probable error of $\pm 6''$ when using a refractometer telescope magnifying only about 2 times, even when the objective is stopped down to an aperture 1 mm in diameter.

The *accuracy* of optical settings is a different matter. The effective telescope apertures used on Abbe refractometers are sometimes necessarily small, especially when the index of the sample does not differ greatly from that of the block. Also, since it is desirable to use a minimum of contact liquid for solid samples, the effective area is often of irregular shape. Thus it is probable that the optical

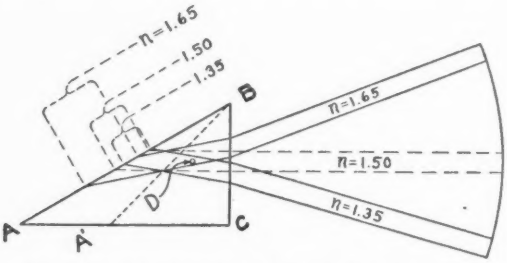

FIGURE 4.—*Mounting of refractometer block with respect to axis of rotation.*

If the image $A'B$ of the AB surface, after refraction by the BC surface, is very near the axis, D, the differences in location of the effective contact areas for various samples are very small, but the telescope aperture may not be filled for high-index samples. If the BC surface is very near the axis, the effective emergent areas coincide approximately, but the contact areas differ. As the effective areas approach A the shielding angle (see fig. 6) increases.

system of the refractometer may be used unsymmetrically with respect to a plane including the optical axis of the telescope and parallel to the refracting edge of the prism. For accuracy under such conditions the telescope must be satisfactorily free from spherical and chromatic aberration, and the eyepiece must be focused accurately for imagery in the focal plane of the objective. Moreover, the refracting prism and the Amici prisms must have optically flat surfaces because, otherwise, there will exist variable refracting angles when various prism aperatures are used.

The principle of symmetrical use of all apertures,[10] so useful in eliminating errors due to aberration, focusing, and curvature of prism surfaces when making index measurement by means of a spectrometer, can not be applied with complete success in commercial refractometry. For example, the refractometer block (refracting prism) can, even for monochromatic light, be correctly installed for symmetrical use with samples of only one particular index. Figure 4 is drawn to facilitate consideration of this question. If either surface of the refractometer block is slightly spherical, a variation in effective refracting angle of the block occurs as slight changes are made in the location of the sample on the face of the block. If at the circumference of an area 1 cm in diameter on the block surface the departure from a plane tangent at the midpoint of the area is only $\lambda/4$, the change in angle can be fully $\pm 10''$ (equivalent to $\pm 5 \times 10^{-5}$ in index of sample) if the displacements of effective aperture can amount to ± 5 mm. This is a matter often

[10] J. Guild, Dictionary of Applied Physics **4**, 113 (MacMillan & Co., Ltd., London, 1923).
L. W. Tilton, BS J. Research **11**, 25–57 (1933) RP575.

overlooked, especially for the small surface of the block from which the rays emerge to the compensator. Since spherical departures from planeness vary as the square of the displacement along a surface, it follows that for equally curved surfaces the prism should be so mounted with respect to the axis of rotation that approximately

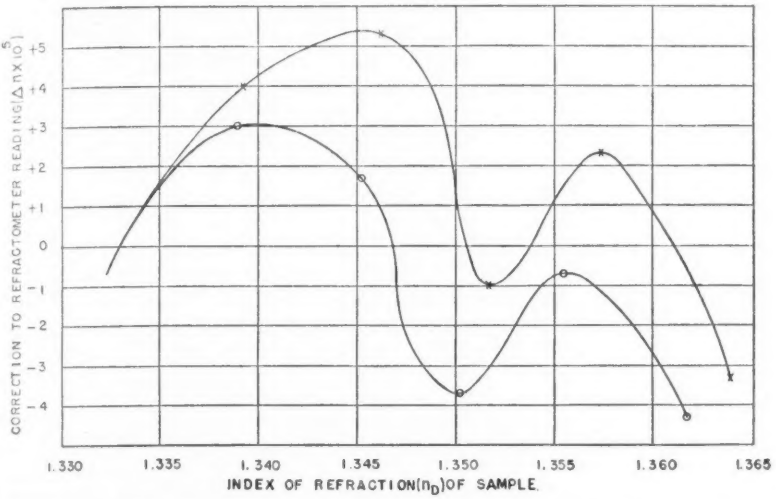

FIGURE 5.—*Correction curves showing the systematic nature of small errors in performance of very good dipping refractometers.*

Each curve is an average for the "*A*" prism of three instruments made by the same manufacturer.

equal displacements of effective aperture shall occur at each polished face of the block. Fortunately, there are some chances of compensating effects. For example, if both prism-surface apertures shift equal distances in opposite directions with respect to the refracting edge, there will be no change in refracting angle, provided the surface curvatures are of like sign and are equal in magnitude.

It seems possible that effects attributable to asymmetrical or extra-axial use of apertures may account for certain systematic errors in the performance of some instruments such as dipping refractometers that have focal-plane scales. The errors for the best dipping refractometers are such that corrections of $\pm 4 \times 10^{-5}$ in index are required as shown in figure 5 for the product of two different manufacturers.

III. TEMPERATURE EFFECTS

It is well known that the average decrease in refractive index of liquids is about 4×10^{-4} per degree centigrade increase in temperature, and it is recognized that temperature must be controlled at the required values, within ± 0.1°C, in order to reduce the direct temperature errors to $\pm 5 \times 10^{-5}$ in index. Otherwise, proper corrections must be applied for the direct errors in index measurements that are caused by the differences between observed and required temperatures. The refractive indices of glasses and other solids are also, although

less sensitively, functions of temperature, and thus one cannot entirely neglect temperature control or correction for the direct errors that occur in their measurement.

Of importance also, but seldom mentioned, is the effect of temperature on the blocks or prisms of glass that are the essential parts of refractometers. In this way, somewhat indirect errors are caused whenever refractometers are used at temperatures other than those for which they are designed or calibrated. Futhermore, the refraction of the emergent rays, on which refractometer settings are actually made, varies slightly with the temperature and pressure of the air and, consequently, in view of the increasing interest in precise refractometry, it may be necessary for clearness to distinguish between indices referred to air at a standard temperature, t_0, and those referred to air at the temperature of observation, t.

1. REFRACTOMETER BLOCK

When using a refractometer at other than optimum working temperature to determine the refractive index of a sample, the indirect thermal errors depend primarily upon the temperature of the glass block of the refractometer and to a slight extent upon the temperature and pressure of the air at the emergence face of the block. Also, if a compensator is used, there will be variations in the extent to which it will deviate rays of wavelength 5893 angstroms. Quantitative discussion starts with the general equation for critical-angle refractometry,

$$\bar{n}=\sin A\sqrt{\bar{N}^2-\mu^2\sin^2\vartheta_2'}+\mu\cos A\sin\vartheta_2', \tag{1}$$

where $\bar{n}$ is the absolute index of the sample; A and $\bar{N}$ are, respectively, the refracting angle and absolute index of the block; μ is the index of the air at the emergence face; and ϑ_2' is the emergent angle (positive if emergence be toward the refracting edge). The relative (to air at $t°$ C) index of refraction, $n=\bar{n}/\mu$, for a sample is expressed as

$$n=\sin A\sqrt{N^2-\sin^2\vartheta_2'}+\cos A\sin\vartheta_2', \tag{2}$$

which is merely equation 1 after division by μ, the index of air at $t°$ C, and replacement of $\bar{N}/\mu$ by N.

From equation 2, after partial differentiation with respect to N and neglecting higher orders, there may be obtained, for finite differences, the equation

$$\frac{\Delta n}{\Delta N}=\frac{N\sin A}{\sqrt{N^2-\sin^2\vartheta_2'}}, \tag{3}$$

from which one may compute the error Δn in the relative (to air at $t°$ C) index, n_t, caused by taking readings from a refractometer table or scale that is correct for N at a standard temperature t_0 and not for the existing $N+\Delta N$ at temperature t. Note that the observed ϑ_2', dependent on N and μ, which change with t, corresponds automatically to the existing $N+\Delta N$ at temperature t and to the existing μ. Thus the assumption of constancy for ϑ_2' with respect to N is justified, and with respect to μ the constancy is justified if the air at the emergence face is also at t. The ratio $\Delta n/\Delta N$ has its minimum value, namely

sin A, for a sample with $n=N \sin A$ (which is the condition for normal emergence, namely $\vartheta_2'=\vartheta_2=0$ and $\vartheta_1'=A$) and since, for the usual Abbe-type refractometer, ϑ_2' does not exceed approximately $\pm 25°$, the ratio $\Delta n/\Delta N$ never exceeds sin A by more than a few parts in a hundred. Consequently, this important error in determining the relative index of any sample at temperature t with respect to air at the same temperature is fairly well represented as

$$\Delta n = \sin A(t-t_0)\Delta N, \tag{4}$$

provided ΔN is now the temperature coefficient of relative index of the refractometer block.

From equation 1, after partial differentiation with respect to N and setting $\mu^2=1$, there is obtained the equation

$$\frac{\Delta \overline{n}}{\Delta \overline{N}} = \frac{\overline{N} \sin A}{\sqrt{\overline{N}^2 - \sin^2 \vartheta_2}}, \tag{5}$$

from which one may compute the error, $\Delta \overline{n}$, in the absolute index, or the error, Δn_{at_0}, in the relative (to air at t_0) index, n_{at_0}, caused when using a refractometer at t °C. Here the index of the sample at t is referred to air at t_0 (thus its temperature coefficient of index, Δn_{at_0}, is identical with $\Delta \overline{n}$, the temperature coefficient of absolute index of the sample) and the fact that ϑ_2' may be measured in air not at t_0, but perhaps at t, has been ignored. Apparently this is the basis on which it is sometimes customary to write and use values of $\Delta \overline{N}$ rather than ΔN in the practical application of equations such as 4 or 5.

For the Pulfrich refractometer, equation 5 becomes $\Delta \overline{n} = (\overline{N}/\overline{n})\Delta \overline{N}$, and the manufacturers have recommended temperature corrections computed as $\Delta n_{at_{20}} \equiv \Delta \overline{n} = (N/n)\Delta \overline{N}(t-20)$. If, however, it is desired that the measured indices refer to air at t, then values of ΔN should be used instead of $\Delta \overline{N}$. In table 2, on lines designated by roman numerals, there are listed (positive) values of ΔN and $\Delta \overline{N} \times 10^5$, for the spectral lines C, D, F, G', and h, that apply to the three 90° blocks that are customarily used on the Pulfrich refractometer. Other listings relate to 60° blocks on Abbe-type refractometers and to similar glasses. Approximate values for other wavelengths may be obtained by linear interpolation. These data should be used, in the absence of more specific information, when applying equations 4 or 5 for estimating corrections to refractometer readings made at t °C. It should be noted that glasses having similar indices and dispersions do not necessarily have similar temperature coefficients of index.

2. AIR AT EMERGENCE FACE

In order to investigate the extent to which it is permissible to ignore the temperature and pressure of the air at the emergence face of the prism, equation 1 is differentiated, partially with respect to μ, and after dividing the right-hand member by μ, one may write

$$\frac{\Delta \overline{n}}{\Delta \mu} = \frac{n \cos A - \sin \vartheta_2'}{n \csc \vartheta_2' - \cos A}, \tag{6}$$

TABLE 2.—*Temperature coefficients[a] of relative* (ΔN) *and absolute* ($\Delta \overline{N}$) *index of refraction (units of fifth decimal) for refractometer blocks and similar glasses at room temperatures*

Highest index measurable	Block		$t+t_0$ / 2	λ=6563 A		λ=5893 A		λ=4861 A		λ=4340 A		λ=4047 A	
	N_D	ν[a]		ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$	ΔN	$\Delta \overline{N}$
	1.5045	64.7	30°	0.29	0.16	0.32	0.19	0.38	0.25	0.44	0.31	.....	.....
	1.5175	64.2	35°	.16	.03	.17	.04	.22	.09	.25	.12	0.28	0.15
1.50	1.5220	58.5	28°	.17	.04	.19	.06	.24	.11	.27	.14	.30	.17
	1.5202	59.6	30°	.34	.21	.35	.22	.40	.27	.44	.31	.48	.35
(I_b) 1.613	1.6220 R, Z	35.9	55°	.....	.24	.....	.28	.....	.39	.....	.50	.....	.....
	1.6227	55.6	33°	.33	.19	.34	.20	.38	.24	.44	.30	.48	.34
	1.6561	33.2	35°	.44	.30	.46	.32	.60	.46	.75	.61	.92	.78
1.70	1.7167	29.4	28°	.66	.51	.74	.59	.94	.79	1.14	.99	1.33	1.17
(II_b) 1.713	1.7474 R, Z	27.8	57°	.....	.70	.....	.78	.....	1.05	.....	1.31	.....	.....
(II_c) 1.746	1.7548	27.6	30°	.77	.62	.85	.70	1.12	0.96	1.36	1.20	.....	.....
	1.7537	27.6	30°	.70	.55	.81	.66	1.09	.93	1.34	1.18	.....	.....
1.75	1.7619	27.1	26°	.77	.62	.86	.71	1.17	1.01	1.43	1.27	.....	.....
(III_b) 1.899	1.9068 R, Z	21.7	?	.....	1.03	.....	1.21	.....	1.71	.....	2.26	.....	.....
(III_c) 1.910	1.9180	21.0	30°	1.12	0.95	1.30	1.13	1.83	1.66	2.44	2.27	.....	.....

[a] With the exceptions noted, the coefficients were determined with the apparatus described in J. Research NBS **17**, 389 (1936) RP919.

R, Z These coefficients of $\Delta \overline{N}$ as listed on p. 37 of Refraktometrisches Hilfsbuch, by W. A. Roth and F. Eisenlohr (Leipzig, 1911), are almost identical with those recommended by Carl Zeiss for their Pulfrich refractometer. For block I these values are those found by C. Pulfrich, Ann. Physik **45**, 609–65 (1892), for Jena glass O. 544 over the range 11° to 99° C; similarly for block II, they list Pulfrich's values for glass O. 165 over the range 14° to 100° C. Their values for block III agree with interpolations between those found by J. O. Reed, Ann. Physik **65**, 707–41 (1898), for glasses O. 163 and S. 57.

[a] Abbe's value, $\nu=(N_D-1)/(N_F-N_C)$, is the reciprocal of the relative mean dispersion.

from which it can be shown that index of sample, as observed by use of a refractometer, is independent of the air at the emergence face when $\vartheta_2'=0$, and also for the unimportant case when $\overline{n}=\overline{N}$. For refractometers with $A=60°$ and for extreme cases with $\vartheta_2'=\pm 30°$, equation 6 becomes

$$\frac{\Delta \overline{n}}{\Delta \mu}=\frac{n-1}{4n-1} \text{ or } -\frac{n+1}{4n+1}, \tag{7}$$

and the ratio $\Delta \overline{n}/\Delta \mu$ varies from $+0.12$ to -0.37 as n varies from approximately 1.7 to 1.3. Since $\Delta \mu=-0.94\times 10^{-6}$ per degree centigrade at room temperature, it is evident that changes of less than $\pm 88°$ in air temperature at the emergence face of the prism on the usual type of Abbe refractometer cannot cause error in excess of $\pm 1\times 10^{-5}$ in measuring samples with indices of 1.7. A corresponding change of $\pm 29°$ C applies for samples with indices of 1.3

For refractometers having blocks with larger refracting angles the tolerances are somewhat less liberal. With a 90° block, as on the Pulfrich refractometer, the right hand of equation 6 becomes $-(\sin^2 \vartheta_2')/n$. Evidently for a ϑ_2' of $-74°$, which occurs when measuring a sample of index 1.30, or 1.47, or 1.66, depending on the particular block that is used, the corresponding tolerances in air temperature at the emergence face are $\pm 15°$, $\pm 17°$, and $\pm 19°$ C, respectively.

To some extent, then, an Abbe-type refractometer, for which $\vartheta_2'=0$ at or near the middle of its index range, is more nearly independent of room temperature than is the Pulfrich type. As a practical matter it is probable that the effect of temperature of air at the emergence face of a refractometer prism is always negligible when one uses a water jacket that partially surrounds the block but not the whole instru-

ment. If the warmer or cooler air can be considered as distributed in successive parallel layers adjacent to the emergence face of the block, then the effective observed ϑ_2' will be determined by room temperature. This view is in accord with the customary practice of using $\Delta\bar{N}$ rather than ΔN in equation 4; thus obtaining a correct n at t referred to air at or near t_0. It is not clear, however, why n should be expressed in this manner. Such relative indices are lower than indices referred to air at t by approximately 1×10^{-5} for every 7° of the excess of t over t_0.[11]

3. COMPENSATOR

The effect of temperature on the compensator of an Abbe refractometer is seldom mentioned. For sodium-lines indices read on Hilger refractometers of the Abbe type at temperatures other than 20° C, the manufacturers recommend a correction, R, expressed in units of the fifth decimal place, as

$$R=r_1(t_1-20)+r_2d(t_2-20), \tag{8}$$

where t_1 and t_2, are, respectively, the temperatures of the Abbe prisms and of the compensator prisms in degrees centigrade, and d is the achromatization reading on a compensator drum having in each quadrant 25 unequal graduations proportional to the cosine of the angular orientation of the compensator. Hilger's accompanying tabulated values of r_1, are the values of $\Delta\bar{n}$ for sodium light that can be computed from equation 5 of this paper. The tabulated values of r_2 vary from 0.062 to 0.018 as n varies from 1.30 to 1.70 and thus, according to the Hilger recommendation, and assuming unusual cases with maximum drum readings of 25, a correction of 10×10^{-5} in index should be added for each temperature rise of from 7° to 22° C of the compensator.

4. ELIMINATION OF COMBINED EFFECTS

There may be some uncertainty in obtaining a suitable value of ΔN, even with the aid of table 2, for use in equation 4 or 5 and, nearly always, there is considerable doubt about values of r_1, r_2, and t_2 for equation 8. Also, there are other sources of uncertainty when using refractometers at other than room temperatures. The temperature distribution in the block may not be uniform and, in addition to causing a variable N, the temperature gradients may temporarily change the refracting angle of the block in an almost unpredictable manner to an extent that may nullify or double the computed corrections. Consequently, it is advisable in precise critical-angle refractometry at other than room temperatures to use a comparison series of standard refractive-index samples for which the indices are known over a range of temperatures and to correct all results on unknowns according to experience with the known samples.

IV. EFFECTIVE WAVELENGTH OF SODIUM LINES

For the most accurate work on a carefully calibrated Pulfrich or other spectral-line refractometer, separation of the D_1 (λ=5896 A) and D_2 (λ=5890 A) lines should, whenever possible, be obtained by

[11] Changes in temperature of air of index μ result in changes in relative index n of a referred medium, according to the equation $\Delta n=\bar{n}\alpha\,(\mu-1)\,(t-t_0)/(1+\alpha t_0)$, where $\alpha=1/270$. See J. Research NBS **14**, 397-400 1935) RP 776.

using a slit or knife-edge provided for such purposes, and either D_1 or D_2 may be measured as desired.[12] Obviously, either the tables used or the scale of the instrument must apply to the particular line measured; otherwise corrections must be known or determined. It should also be remembered that the relative positions of D_1 and D_2 in the field of view are reversed whenever the dispersion of the sample exceeds that of the block.

When the D lines are easily resolvable but not separated with a slit or knife-edge, the critical border at the edge of the dark part of the field usually corresponds to D_1 for samples having smaller dispersions and always corresponds to D_2 for samples having larger dispersions than that of the reference block.[13] Ordinarily, however, the critical edges for D_1 and D_2 are not separated by use of a slit or knife edge and often they are so near the limit of resolution that they are seen as a blurred or soft region instead of a sharp edge. Then, according to Guild, one sets on something intermediate between D_1 and D_2. The exact results obtained probably vary with the observer and with the nearness of approach to the limit of resolution, but it would seem that tables usually furnished by the makers, and probably approximately correct for the arithmetic mean of the D lines (D_m, $\lambda=5893$ A), are suitable for use with readings made under these circumstances. The fact that refractometers are used for substances having various dispersions, some larger and some smaller than that of the refractometer block, adds weight to the argument that the scales and tables should be computed for D_m, especially if only one scale or table is provided with a given instrument.

Conditions are more complicated in using white light to measure D-lines indices with an Abbe refractometer or with some of its variants, such as the dipping or immersion type. In all standard Abbe instruments reading by estimation to the fourth decimal place, the whole matter is irrelevant because the index difference (D_m-D_1) seldom if ever exceeds 1×10^{-4} for media having indices of 1.7 or less. A corresponding statement is true for dipping refractometers with index ranges below 1.5 approximately. On the upper index ranges of Abbe refractometers reading to the fifth decimal and on dipping refractometers with high-index prisms, the actual setting for the nominal D-line index is, strictly speaking, influenced slightly by the way in which the compensator functions. It is very difficult to make the combined Amici prisms nondeviating for sodium light with sufficient accuracy for fifth-decimal-place measurements. Fortunately, the question of whether a compensator is more nearly nondeviating for D_1, D_m, or D_2 is not as important as it is to know just which of these wavelengths was used in computing a scale or table of equivalents and then to adjust and use the instrument accordingly. The actual deviation is of less importance because, first, not all of the deviation of a compensator gives rise to effective error,[14] and second, a portion of the effective error is tantamount to a change in length of a scale

[12] See discussion by J. Guild, Proc. Phys. Soc. (London) **30,** 162 (1918) or Nat. Phys. Lab., Collected Researches **14,** 276 (1920).

[13] If the ratio $(n_F-n_C)/(N_F-N_C)$ is lower than the ratio $(N\tan A)/[n\tan A+(N^2-n^2)^{\frac{1}{2}}]$, then the critical border corresponds to D_1. The second of these ratios reduces to n/N for a sample that yields normal emergence from the refractometer block.

[14] Sometimes only relatively small orientations of the compensator are required in order to effect achromatizations for a wide variety of samples, and in other instances the particular class of samples to be measured may achromatize within a very narrow range of drum readings.

and thus is compensatable in making the scale or the table of equivalents.

V. CONTACT LIQUID

The permissible degree of prism in the contact liquid between sample and refractometer block can be conveniently specified in terms of interference fringes. For two successive fringes separated by any distance, a, in a prismatic layer of liquid having a very small refracting angle, ϕ, and refractive index, n_1, the difference in optical path differences is expressible as $\lambda = 2n_1 \Delta t \cos\theta$, where λ is the wavelength in air, $\Delta t = \phi a$ is the difference in thickness for any distance a, and θ is the angle of refraction in the film. Hence, an expression for the number of fringes per unit length of the film is $1/a = (2n_1\phi \cos\theta)/\lambda$. Guild has quantitatively discussed the relation of film angle to the error, Δn, in refractive-index measurement of a sample and finds $\phi = \Delta n/n_1(1-n^2/n_1^2)^{\frac{1}{2}}$. Consequently, the general expression for tolerance in number of fringes per unit length corresponding to an error of 1×10^{-5} in refractive-index measurement is

$$T_{(fringes)} = \frac{2\times10^{-5}\cos\theta}{\lambda(1-n^2/n_1^2)^{\frac{1}{2}}}. \tag{9}$$

If fringes are formed by light that enters the film at nearly normal incidence, $\cos\theta$ is essentially 1, and the number of fringes per unit length is greater than for other conditions. Also, the number of permissible fringes, when formed in this manner, increases as n_1 is chosen more nearly equal to n. Thus, for example, if an observer uses monobromnapthalene as contact liquid when measuring the index of lithium fluoride, 1.39, or of borosilicate crown glass, 1.52, the maximum tolerances in permissible fringes per centimeter when applying the sample to the refractometer block are 0.6 and 0.8 fringes, respectively, for an error of $\pm1\times10^{-5}$ in index measurement. If, however, one chooses a light oil with index of 1.45 when measuring the lithium fluoride, and ethylene bromide with index 1.54 when measuring the crown glass, then the tolerances per centimeter become 1.2 and 2 fringes, respectively.

In best practice, however, the light enters at grazing incidence, the angle of refraction is critical, $\sin\theta = n/n_1$, and thus from equation 9 the tolerance in number of fringes as viewed in the exit pupil is found to be constant for a given wavelength, namely, one-third fringe per centimeter for yellow light.

The possible effect of contact liquid on the cement that holds the refracting prism in its metal water jacket must be considered in precise refractometry. Accumulating evidence indicates that dimensional changes in the cement can cause fluctuating variations in the angular relationship between prism and scale that render the fifth decimal place in refractive index of no value. Since this type of error was first noticed by the writer, reports from another laboratory seem to confirm this opinion. When using successive solid samples it is probable that various degrees of partial saturation can exist in the cement, and thus the resulting errors in index readings are variable. On the other hand, when measuring the index of liquids it is probable that saturation reaches approximate equilibrium, especially after requisite purity in situ has been maintained by repeated samplings and consequent thorough leeching of the cement.

These views are in accord with the possibility of a short-term repeatability for liquids that may explain a growing demand for calibrations and standardizations with liquid samples, regardless of their very high temperature coefficients, ease of contamination, and possible instability. Actually, however, it seems that liquids having identical index, but differing in their effects on the cement, might give different index readings. Thus the accuracy of results with liquids is even more questionable than has previously been supposed, unless a solid sample is used before, during, and after successive saturations and dryings of the cement. Obviously, since various contact liquids may differ in their effects on the cement, it is advisable to use caution in changing from one to another during a given calibration or series of measurements, and it is desirable to ascertain what contact liquids have minimal effects on the cement used on a particular instrument. Also, it is evident that the cements used by manufacturers on precision refractometers should be carefully selected for minimum susceptability to dimensional changes.

VI. SHIELDING

When using solid samples the rays at truly grazing incidence in the sample may not exist because of improper extent or location of the source, improper preparation of sample, excess of contact liquid, or because the contact surfaces are below the level of the adjacent cement or metal.

Shielding of the rays that might be critically refracted can occur even when working with liquids. Since the liquid layer of the sample must have finite thickness and also be limited in its extent, the limiting rays cannot be truly grazing but are necessarily shielded in some degree, as illustrated in figure 6. Abbe shows that when the actual angle of incidence in the liquid is $[(\pi/2)-E]$ the index determined is erroneously low by $nE^2/2$. Thus with a shielding angle $E=25'$ (i. e., 0.0073 radians) and for $n=1.7$, the resulting error is less than 5×10^{-5}. Assuming the layer of sample is as thick as 0.10 or 0.15 mm, the shielding angle cannot be as large as 25′ provided the ray paths in the sample are as long as 14 and 21 mm, respectively.[15] To reduce this error to 1×10^{-5} when using those thicknesses, the corresponding ray paths must be 29 and 43 mm. Possibly, however, there is sufficient multiple internal reflection and scattering to produce some illumination at truly grazing incidence. Otherwise it would seem necessary, or at least advantageous, in the design of refractometers for precise measurements, to provide ample length of the hypotenuse faces of the Abbe prisms. In any case it is advisable to use sufficient liquid to permit transmission over a goodly portion of the prism face even though the effective aperture is small.

VII. HERSCHEL FRINGES

A troublesome phenomenon in precise refractometry of liquids is the production of Herschel interference fringes in the thin layer of liquid between the Abbe prisms. These fringes are observable in the telescope as narrow dark bands in the light half of the field, and there is danger that some of them may be so close to the critical border

[15] A corresponding shielding error ascribable to the curvature of the contact surface of solid samples is almost negligible if the contact surface merely approximates optical planeness.

as to appear continuous therewith. The consequent errors are maximal for lowest index liquids.

Originally, both prisms of the Abbe refractometer had polished surfaces and Abbe[16] relied entirely on adequate prism separation for the avoidance of these interference fringes. Later, Pulfrich[17] in-

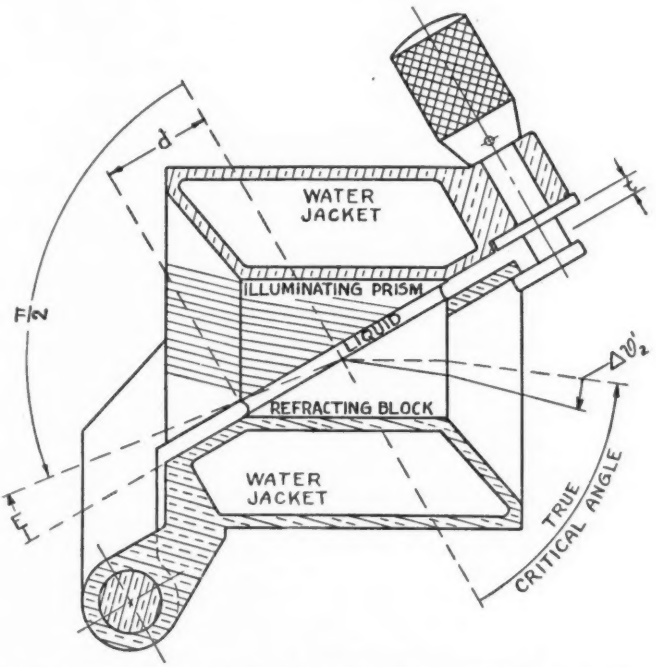

FIGURE 6.—*Geometrical shielding of critical rays caused by separation of Abbe prisms.*

For a sample thickness, t, of 0.10 mm (greatly exaggerated here) the distance, d, from effective aperture to edge of ground-glass surface must be 14 mm or more in order that the shielding angle, E, shall not exceed 25′, and the resultant error in emergent rays, ϑ'_2, shall not exceed 5×10^{-4} in refractive index.

troduced a modification by fine-grinding the surface of the illuminating prism in order to avoid well-defined and disturbing images of the source and also to avoid the interference fringes with which he associated the name of Mascart.

If, however, the surface of the illuminating prism is too finely ground, or if it lies too near the polished surface of the refracting prism when the two prisms are clamped together for use with liquid samples, then Herschel interference fringes may still be visible in the light half of the field near the critical edge or border. These fringes are formed by interference between directly transmitted light and light that is multiply reflected between the prism surfaces at angles very near the critical value. The finer the grinding, the sharper is the contrast between the light and dark fringes.[18] The closer the prism surfaces and the lower the optical density of the intervening liquid

[16] Gesammelte Abhandlungen von Ernst Abbe, **II**, 149, 150 (Gustav Fischer, Jena, 1906).
[17] Z. Instrumentenk. **18**, 107 (1898).
[18] See E. Gehrcke, Handbuch der Physikalischen Optik **1**, 392 (Johann Ambrosius Barth, Leipzig, 1927).

layer, the greater is the distance between successive bright fringes and from the true edge to the first bright fringe. The width, separation, and visibility of the fringes varies, also, with the degree of inclination of the prism surfaces. Consequently, in many refractometers of the double-prism type the true edge is masked and cannot be distinguished from the edge of the first or some succeeding bright fringe. Under these conditions an instrument calibrated for solid samples may not be equally satisfactory for work on liquids of low index of refraction. The resulting errors (negative), however, seldom exceed about -3×10^{-4} in index.

The Herschel fringes can be avoided by the use of large prism-surface separations, say 0.1 mm or larger, but (aside from the danger of shielding, see fig. 6) this is not always satisfactory except for somewhat viscous liquids. For use when it is necessary to retain thin or volatile liquids, it would be desirable to have the prism pair set with a very thin intervening space, perhaps 0.03 mm. Abbe [19] mentions as upper limits of prism separation about 0.05 to 0.10 mm; values that can with comparative safety be used without geometrical shielding of the critical border line or the presence of fringes. He used, also, films as thin as 0.03 to 0.05 mm. On 10 Abbe refractometers used at the National Bureau of Standards, including instruments from 5 different makers, the prism separations range from 0.02 to 0.21 mm. In several of these instruments narrow Herschel fringes are distinctly observable.

From experiments at this Bureau with various auxiliary illuminating prisms, all set as close to the refracting prism as was possible without clamping, it was found that silicon carbide abrasives (carborundum) numbered 100 or coarser are satisfactory for making illuminating prisms that give true critical borders. Carborundums numbered 150 and 220 were found almost satisfactory, the traces of the fringes being so faint that they seemed unlikely to cause any trouble. Carborundums *F* and *FF*, however, proved unsatisfactory for such extremely close prism settings. Likewise, emery in sizes numbered 140 and 200 (standard mesh) and 302 and 304 (Am. Optical Co.) were tried without success in seeking a fine-ground flat surface that can be set very close to the refracting prism without the production of fringes or other shielding effects to an extent that is fatal for accurate fifth-decimal-place refractometry.

Coarsely ground surfaces are, however, somewhat objectionable in this connection, because they are not easily and thoroughly cleaned between successive applications of a series of liquid samples. Trials with concavely surfaced lenses as illuminating prisms showed that the character of the fringes was favorably changed by slight curvatures, perhaps because the greater glass separations permitted greater thickness of the liquid layer at the effective aperture. Consequently, the use of concave surfaces made with the finer abrasives was tried. With emery numbered 140, 200, and 302, cylindrical surfaces with axes lengthwise of the illuminating prism and with radii of 525 mm, were successively ground and found entirely satisfactory. Also, with emery 302 a similar surface having a radius of 1,050 mm was made and found almost satisfactory. The prism width used in these experiments was 18 mm, and the maximum prism separations along

[19] Gesammelte Abhandlungen von Ernst Abbe, **II**, 150. (Gustav Fischer, Jena, 1906).

the axes of the surfaces are therefore approximately 0.08 and 0.04 mm for the curvatures mentioned.

After the above-described preliminary experiments the prism of a fifth-decimal-place refractometer was ground with 150 emery on a cylindrical tool with a 700-mm radius and the lateral edges flattened for a width of 1.5 mm on each side. This illuminating prism was set so that when clamped the flattened lateral edges were about 0.02 or 0.03 mm from the polished face of the refracting prism. The maximum separation along the axis of the ground surface was then about 0.05 mm, or 0.002 in. While this value is perhaps a little greater than desired when the ground surface is flat, it is found to be more or less satisfactory under these conditions for briefly retaining liquids such as ether, alcohol, and hexane, provided a sufficiently large sample of the liquid be applied. However, with small samples, or after partial evaporation takes place, no satisfactory edge is obtained.

VIII. SUMMARY

Those sources of error that have been quantitatively treated in this paper are briefly summarized in table 3, together with tolerances that correspond in each individual case to an error of $\pm 1\times10^{-5}$ in refractive index of sample (instead of $\pm 5\times10^{-5}$ that has been frequently used in the text). Sources numbered 1, 2, 5, 6, 7, and 12 are primarily of interest in the construction of refractometers. Number 9 can, almost always, be neglected. The user should, at least once, consider 7, 12, and also the possibility of compensator defects, for each instrument that he uses. Those requiring almost constant attention are 3, 4, 8, 10, 11, and, of course, the possibility of the shielding of those rays that alone can correspond to critical-angle phenomena.

TABLE 3.—*Summary of sources of refractometer error that have been quantitatively discussed*

Page of this paper	Source number	Quantity evaluated or controlled			Plus or minus tolerances for various indices of sample ($\Delta n=\pm1\times10^{-5}$; Abbe-type refractometer, $A=60°$ and $N=1.75$, unless otherwise noted)			
		Name	Symbol	Unit	$n=1.3$	$n=1.5$	$n=1.7$	Provisory remarks
312	1	Index of block	ΔN		0.00001	0.00001	0.00001	
313	2	Angle of block	ΔA	Seconds of arc.	1.8	2.3	5.0	For all values of A.
313	3	Zero adjustment	Δn		0.00001	0.00001	0.00003	Test slab of $n=1.5$.
313	4	Prism orientation	$\Delta\vartheta'_2$	Seconds of arc.	3	4	10	
313	5	Position of scale ruling		Microns	1.9	2.3	5.6	12-cm scale arm.
313	6	Linear eccentricity		do	5		11	Correct adjustment at $n=1.5$.
316	7	Block surface sagitta[1]		λ	0.04	0.05	0.10	±5-mm displacements.
319	8	Block temperature	Δt_N	°C	1.5°	1.5°	1.4°	
320	9	Air temperature	Δt_a	°C	29°	Very large	88°	Abbe; $A=60°$; $N=1.75$.
320	9	do	Δt_a	°C	15°	17°	19°	Pulfrich; $A=90°$; $\vartheta'_2=74°$.
321	10	Compensator temperature	Δt_c	°C	0.64°	0.85°	2.2°	Hilger; maximum compensation.
323	11	Contact wedge	ϕ	Fringes/cm	.3	.3	0.3	Viewed in exit pupil.
324	12	Shielding angle	E	Minutes of arc.	13.5	12.5	12	

[1] For an area 1 cm in diameter.

After careful experiments extending over a period of years and involving much testing and other precise work on numerous refractometers of various kinds and makes, including the Pulfrich and the dipping types, the writer is unable to say that he has attained an accuracy better than ± 2 or 3×10^{-5} in critical-angle refractometry of solid samples on commercial instruments.[20] In fact, speaking only of precision, it has often seemed impossible to do better than ± 1 or 2×10^{-5}, even when merely repeating observations with the same solid sample on a given instrument after independently resetting the fringes for the elimination of wedge effect in the contact liquid. These statements do not relate entirely to "single observations" but sometimes refer to the means of four or more scale readings (the number depending on the sensitivity of the particular instrument) made after as many settings of the cross hairs on the critical border. Thus these estimates of accuracy and precision are to a large extent independent of the ordinary accidental errors of settings and readings. Moreover, they refer to work done with considerable care in order to eliminate systematic error. More or less attention has at times been given to temperature effects, nature of contact liquid, shielding effect of excess contact liquid, orientation of fringes, width of fringes, location of effective area of contact on face of block, curvature of sample surface, curvature of block faces, curvature of faces of Amici prisms, chromatic parallax, spherical aberration, etc., without finding that any one of them seemed especially pertinent to the problem at hand. Probably, then, it is the combined effect of a number of these sources of error that occasionally can cause sufficient trouble to prevent the consistent attainment of a higher precision and accuracy that sometimes seems almost within reach.

WASHINGTON, February 12, 1943.

[20] The errors and imprecisions experienced in the refractometry of very small samples of liquid are, on the average, larger than those found for work on solid media. This is probably because of the higher temperature effects and the difficulty of preventing contamination.

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NATURE OF THE PRISMATIC DARK INTERSTITIAL MATERIAL IN PORTLAND CEMENT CLINKER

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ABSTRACT

As a result of a series of previous investigations by the phase equilibrium method, it has been concluded that K_2SO_4 and $K_2O.23CaO.12SiO_2$ are the only compounds containing K_2O that may exist when a mixture of K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2, and SO_3, in the proportions occurring in portland cement clinker, is heated and cooled under equilibrium conditions. Frequent observations of a prismatic dark interstitial phase in etched, polished sections of commercial clinker and in rapidly cooled laboratory clinkers led to the present study of the relation of this phase to the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ and to other systems involving K_2O. The prismatic phase has not been found to exist under equilibrium conditions, but has been produced only under conditions of rapid cooling. Both thermal and compositional conditions that have been found to be required for its formation suggest that it may be a metastable form of $3CaO.Al_2O_3$ and monotropic with respect to the stable, isotropic, rectangular $3CaO.Al_2O_3$. That portion of K_2O combined as K_2SO_4 has been found to have no effect in inducing the formation of the prismatic phase. The conditions necessary for the formation of this phase have been outlined. Although the exact composition has not been established definitely, because of the experimental difficulties that have been outlined, the close relationship between the prismatic phase and $3CaO.Al_2O_3$ leads to the recommendation that this phase be referred to as "prismatic $3CaO.Al_2O_3$" instead of the term "prismatic dark interstitial material."

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I. INTRODUCTION

The relatively recent application of the metallographic method of microscopical examination, employing polished and etched specimens, to studies of portland cement clinker has been of great value in obtaining a more exact conception of the types and amounts of the various constituents present.

Certain phases appearing in the matrix between crystals of $3CaO.SiO_2$ and $2CaO.SiO_2$ are distinguished by the relatively rapid rate with which they are etched by water, and have come to be known collectively as "dark interstitial material." Some of these dark interstitial phases are crystalline and can be subdivided into rectangular and prismatic types, both of which are etched readily by water. An amorphous or glassy phase also is included in the dark interstitial group. The readiness with which it is etched by water is determined by its composition. Generally, it is not acted upon to as great a degree as are the crystalline phases of this classification, but in some instances very little difference exists.

In a paper published in 1938, Insley and McMurdie [1][1] report that the rectangular isotropic material is $3CaO.Al_2O_3$ and that the amorphous material is glass. The prismatic crystals were found to have a low double refraction with parallel extinction, and a mean refractive index approximating 1.72. These workers observed that when laboratory mixtures comparable to portland cement in composition were cooled from 1,450° to 1,250° C at a rate of 10° C per minute, only the Na_2O-bearing and the K_2O-bearing samples contained prismatic interstitial crystals similar to those observed in commercial clinker.

A bladed form of $3CaO.Al_2O_3$ was observed by Brown [2] in 1937 in thin sections of certain laboratory clinkers prepared from commercial mixes. This form was explained by Brown as due to a directional crystallization of the $3CaO.Al_2O_3$ conferred by the crystallizing $3CaO.SiO_2$. A bladed form of $3CaO.Al_2O_3$ has been observed by the present author in preparations free of alkali and is distinguished from the prismatic dark interstitial material by an undulatory extinction and the absence of sharp parallel extinction.

No K_2O compound having optical properties similar to those of the prismatic phase has been identified in any of the phase-equilibrium studies of K_2O-containing systems which are related to clinker compositions [3, 4, 5, 6]. The compound $8CaO.Na_2O.3Al_2O_3$, discovered by Brownmiller in the system Na_2O-CaO-Al_2O_3 [7], has the refractive indices: $\alpha=1.702$ and $\lambda=1.710$. It is possible that the presence of Fe_2O_3 raises these indices, because of solid solution, to values similar to those that have been observed for the prismatic phase. The system Na_2O-CaO-Al_2O_3-SiO_2 is now being investigated by Greene of this laboratory. On the basis of present data, it appears that $8CaO.Na_2O.3Al_2O_3$ may be a final product of crystallization along with either or both $2CaO.SiO_2$ and $3CaO.SiO_2$. However, some Na_2O appears to be associated with CaO and SiO_2 in the formation of a ternary compound or in solid solution in $2CaO.SiO_2$ and, in view of the low soda content of most portland cement clinkers, rarely exceeding 1 percent, it is doubtful whether appreciable amounts of $8CaO.Na_2O.3Al_2O_3$ would be found in commerical clinkers.

The purpose of this report is to present data relative to the probable composition of the prismatic dark interstitial material.

[1] Figures in brackets indicate the literature references at the end of this paper.

Included in these data are the results obtained by other investigators on the microscopic structure of commercial clinkers. The relation of the prismatic phase to the system $K_2O.23CaO.12SiO_2$–CaO–$5CaO.3Al_2O_3$ in particular, and to other systems, is discussed.

II. EXPERIMENTAL METHOD

The samples of mixtures used in this study were, in most cases, taken from the base samples employed in connection with phase-equilibrium studies of various systems conducted by the author. The thermal treatment to which the charges were subjected varied and is given in the text.

The microscopical study of the charges included the examination of powders and etched polished sections of all samples. In some cases, etched polished thin sections also were examined.

III. FORMATION OF THE PRISMATIC DARK INTERSTITIAL MATERIAL

1. DATA FROM OTHER SOURCES INDICATING THE NATURE OF THE PRISMATIC PHASE

An analysis was made of data obtained by other investigators in microscopical studies of clinker by the polished-surface method. These data are included in this paper because: (1) Definite suggestions on the nature of the prismatic phase are to be found in the results of the analysis, and (2) those results determined, to some degree, the direction of further study of the problem.

(a) STUDIES BY INSLEY AND OTHERS

In a study of 26 different commercial clinkers, Insley, Flint, Newman, and Swenson [8] report that the rectangular crystalline form of dark interstitial material, which has the optical properties of $3CaO.Al_2O_3$, was found in only 2 samples, and there in only very small amounts. The anisotropic (prismatic) form was a much more abundant constituent, and occurred in all samples examined. In samples with low Al_2O_3:Fe_2O_3 ratio, it was present in very small amounts and in localized clusters, but in samples with higher Al_2O_3:Fe_2O_3 ratio, the prismatic crystals were more abundant and distributed more uniformly.

A portion of the data relative to the prismatic material is reproduced in table 1. Since Insley and McMurdie [1] (and the author also in some preliminary studies) had found that the presence of alkali was necessary for the formation of the prismatic phase, it might be expected that the prismatic material would contain an appreciable amount of the alkali, and that the amount of this material would increase as the amount of alkali in the clinker increases. Examination of their data, however, does not support this conclusion. In fact, the average alkali content of the six clinkers containing the greatest amounts of the prismatic phase, 8 to 14 percent, is only 0.56 percent, whereas the average alkali content for the nine clinkers containing 1 to 6 percent of the prismatic material is 0.92 percent. The lack of relationship between the alkali content and the amount of the prismatic phase is shown graphically in diagram *A* of figure 1.

TABLE 1.—*Data pertaining to the prismatic dark interstitial material in commercial clinker samples*

[Insley, Flint, Newman, and Swenson]

[Order of increasing Al_2O_3: Fe_2O_3 ratio. $C_3A = 3CaO.Al_2O_3$]

Clinker	Al_2O_3: Fe_2O_3 ratio	Al_2O_3	Na_2O	K_2O	Total alkalies	Potential C_3A	Prismatic (dark interstitial)	Glass (amorphous, dark interstitial)
		%	%	%	%	%	%	%
1	0.86	4.20	0.07	0.27	0.34	3.0	½	1½
2	.89	5.35	.04	.19	.23	4.1	<¼	2
3	.91	5.38	.83	.48	1.31	4.3	4	3
4	.91	6.22	.29	.64	0.93	5.1	½	4½
5	.92	5.38	.92	.26	1.18	4.3	1½	2½
6	.92	4.77	.17	.31	0.48	4.1	½	2
7	1.01	5.08	.12	.48	.60	5.1	<¼	2½
8	1.07	4.08	.07	.42	.49	4.7	½	2½
9	1.12	5.77	.18	.16	1.34	6.7	1	2½
10	1.12	5.50	.15	.31	0.46	6.5	½	2
11	1.12	5.50	.13	.46	.59	6.5	½	4½
12	1.12	4.81	.17	.23	.40	5.7	<¼	3
13	1.22	5.38	.07	.23	.30	7.2	1½	1½
14	1.23	6.30	.08	.44	.52	8.3	½	3½
15	1.25	6.33	.11	.66	.77	8.5	1	4
16	1.34	5.37	.15	.56	.71	7.7	½	2½
17	1.73	3.84	.25	.28	.53	6.4	3	2
18	1.78	6.94	.18	.50	.68	12.4	5	4
19	2.07	7.24	.20	.60	.80	13.6	8	9
20	2.11	6.80	.10	.21	.31	12.8	[a] 12	3
21	2.53	7.89	.08	.58	.66	15.9	[a] 11	10
22	2.64	5.22	.30	.43	.73	10.7	6	7
23	2.68	7.85	.14	.62	.76	16.0	14	6
24	2.78	5.55	.34	1.08	1.42	12.4	6	9
25	2.89	6.39	.13	0.14	0.27	13.4	8	10
26	3.73	7.35	.19	.39	.58	16.4	14	4

[a] Rectangular C_3A was observed in very small amounts only in clinkers 20 and 21.

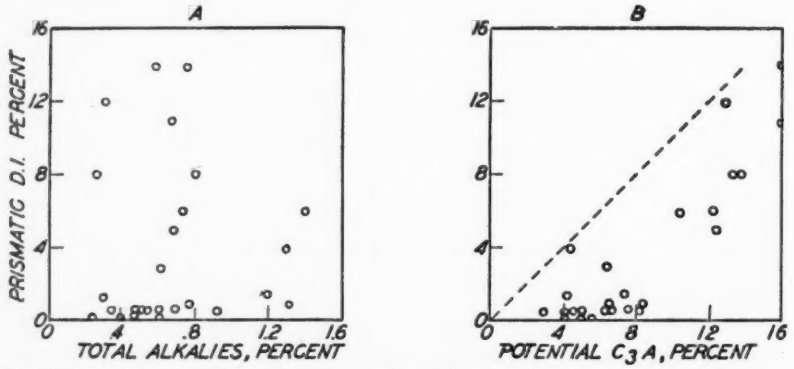

FIGURE 1.—*Relationship between the dark prismatic material and (A) total alkalies and (B) potential* $3CaO.Al_2O_3$.

[From data by Insley.]

Attention is called specifically to clinker 20 (table 1). This clinker contains 0.31 percent of total alkali and also 0.12 percent of SO_3 [8]. Since the K_2O combines preferentially with SO_3 to form K_2SO_4 [6], about 0.17 percent of alkali remains to effect the formation

of the prismatic phase. If all of this alkali were present in the 12 percent of prismatic material, the alkali content of this phase would be only 1.4 percent. Furthermore, in this calculation any alkali that might be in the 3 percent of glass present or in combination with other components is not considered.

There does appear, however, to be a relation between the calculated percentage of $3CaO.Al_2O_3$ present at complete crystalline equilibrium [9] and the amount of prismatic material observed. There is a trend toward increasing amounts of the prismatic phase as the percentage of calculated $3CaO.Al_2O_3$ increases. This relation is shown in diagram *B* of figure 1. The dotted line indicates the limiting amounts of the prismatic material that could be formed if the composition of this phase is essentially that of $3CaO.Al_2O_3$. As is to be expected, the amounts of the prismatic material generally are lower than the potential amount of $3CaO.Al_2O_3$, since varying amounts of glass from which more prismatic material might possibly crystallize were present.

(b) STUDIES BY WARD

In a study of the effect of heat treatment and cooling rate on the microscopic structure of clinker, Ward [10] compared the structure of commercial clinkers as received with that of portions of the same clinker that had been reheated to clinkering temperatures and then cooled; one portion at a rapid rate, and another at a slow rate. These data are given in table 2. The amounts of glass reported are the values determined by a 2-second water-etch followed by etching for 3 seconds in a 1-percent alcoholic HNO_3 solution, and do not include the portion of the glassy phase etched by a KOH solution. The readiness with which a glass is etched by a particular reagent depends upon its composition. A glass low in Fe_2O_3 is readily etched by the treatment just mentioned, but a glass having a high Fe_2O_3 content is unaffected [11]. This type of glass is revealed by etching with a 10-percent KOH solution [12].

As shown in table 2, there is no relation between the percentage of the total alkalies, nor of the Al_2O_3 content, and the percentage of prismatic material. On the other hand, the total amount of the three forms of dark interstitial material (glass, rectangular $3CaO.Al_2O_3$, and prismatic material) bears a relation to the calculated $3CaO.Al_2O_3$ at crystalline equilibrium. The relation of the various types of dark interstitial material to the potential $3CaO.Al_2O_3$ content is plotted in figure 2. Dotted lines to indicate the maximum amounts that could be formed of a phase, sensibly $3CaO.Al_2O_3$ in composition, have been inserted in the diagrams as means for comparison.

Of the 10 slowly cooled clinkers, plotted in diagram *A* of figure 2, 3 show the dark interstitial material to be all prismatic and not rectangular, 1 shows 4 percent of prismatic to 7 percent of the rectangular, and in the remaining 6 the rectangular is rather high and the prismatic is substantially zero. It is interesting to note that each of the first three has an Al_2O_3:Fe_2O_3 ration of less than 1.38, whereas that for each of the last six is well above 1.38. The Al_2O_3:Fe_2O_3 ratio for the one showing both forms is 1.88. The value 1.38 is mentioned because in the quaternary system CaO–Al_2O_3–Fe_2O_3–SiO_2 [13] the course of crystallization has been shown to differ for cements having Al_2O_3:Fe_2O_3 ratios above and below 1.38.

TABLE 2.—*Data pertaining to the dark interstitial material (water-acid etch) in heat-treated and untreated commercial clinkers (Ward)*

[Order of increasing Al_2O_3:Fe_2O_3 ratio. $C_3A = 3CaO.Al_2O_3$]

Clinker [a]	Al_2O_3 corrected for TiO_2	Fe_2O_3 corrected for FeO	Al_2O_3: Fe_2O_3 ratio	Na_2O	K_2O	Total alkalies	Calculated C_3A at cryst. equil.	Rectangular C_3A micro.	Pris. D. I. micro.	Glass micro.	Total D. I.
	%	%		%	%	%	%	%	%	%	%
4S	4.61	7.11	0.65	0.41	0.10	0.57	0.2	0	2	0	2
4P	4.73	5.33	.89	.53	.20	.73	4	0	2	0	2
4Q	4.91	6.04	.81	.37	.12	.49	3	0	0.2	0	0.2
11S	4.24	4.89	.87	.52	.05	.57	3	0	3	1	4
11P	4.54	5.07	.90	.66	.16	.82	3	0	0	3	3
11Q	4.08	4.32	.95	.51	.08	.59	4	0	0	3	3
2S	4.97	5.12	.97	.27	.37	.64	5	0	3	0	3
2P	5.51	5.49	1.01	.33	.71	1.04	5	0	3	0	3
2Q	5.45	4.88	1.12	.24	.30	0.54	6	0	0	3	3
8S	4.86	2.98	1.63	.15	.25	.40	8	7	0.2	0	7.2
8P	4.95	3.02	1.64	.17	.49	.66	8	0	1	6	7
8Q	4.86	2.95	1.65	.10	.08	.18	8	0	0	7	7
10S	4.83	2.88	1.68	.26	.33	.59	8	4	Trace	2	6
10P	4.79	2.86	1.68	.34	.81	1.15	8	0	3	2	5
10Q	4.84	2.89	1.68	.26	.37	0.63	8	0	0.2	6	6.2
6S	5.81	3.08	1.88	.07	Trace	.07	10	6	0	2	8
6P	5.93	3.13	1.89	.10	0.11	.21	11	7	0.6	3	10.6
6Q	5.85	3.11	1.88	.08	.08	.16	10	0	0	9	9
3S	5.09	2.71	1.88	.35	Trace	.35	9	7	4	2	13
3P	5.37	2.24	2.40	.63	0.20	.83	10	0	10	7	17
3Q	5.16	1.98	2.60	.47	.10	.57	10	0	5	10	15
9S	5.59	2.23	2.51	.32	.22	.54	11	10	0	0	10
9P	5.56	2.22	2.51	.38	.54	.92	11	0	2	7	9
9Q	5.59	1.97	2.84	.33	.29	.62	12	0	0	8	8
1S	5.97	2.21	2.70	.10	0.97	1.07	12	12	0	0	12
1P	6.03	2.22	2.71	.10	1.58	1.68	12	0	13	1	14
1Q	5.71	1.90	3.00	.10	1.11	1.21	12	0	2	14	16
7S	6.64	2.35	2.82	.34	0.28	0.62	14	12	0.3	2	14.3
7P	6.85	2.35	2.91	.42	.58	1.00	15	2	7.0	6	15
7Q	6.80	1.96	3.47	.32	.38	0.70	15	0	0.2	14	14.2

[a] S clinkers were reheated and cooled slowly. P clinkers were the commercial products as received. Q clinkers were reheated and cooled quickly.

Of the 10 quickly cooled clinkers the interstitial material is composed principally of the amorphous type. No rectangular $3CaO.Al_2O_3$ is in any clinker and, with the exception of two clinkers, the amount of prismatic material is zero or not more than 0.2 percent. As shown in diagram *B* of figure 2, the amount of the amorphous type (glass) closely approaches the respective values calculated for potential $3CaO.Al_2O_3$.

The effect of variations in cooling conditions on the proportions of the three types of dark interstitial material is evident in the commercial clinkers examined by Ward. In clinkers in which the amount of prismatic material is less than the calculated amount of potential $3CaO.Al_2O_3$, the difference may be accounted for by the presence of the other types. The relation of the amount of the prismatic phase to the other forms of dark interstitial material to the calculated $3CaO.Al_2O_3$ is shown in diagram *C* of figure 2.

In diagram *D* (fig. 2) the total dark interstitial percentages are plotted against the potential $3CaO.Al_2O_3$ contents for all types of clinker. It is seen that the combined amounts of all the phases that are distinguished by the water-acid etch approach the values calculated for

potential $3CaO.Al_2O_3$, indicating that these three types of material do not differ greatly in composition.

The following generalizations may be made in regard to these results.

1. The prismatic material is much more abundant in the plant cooled than in quickly or slowly cooled clinkers.

2. The high glass content of the quickly cooled clinkers suggests

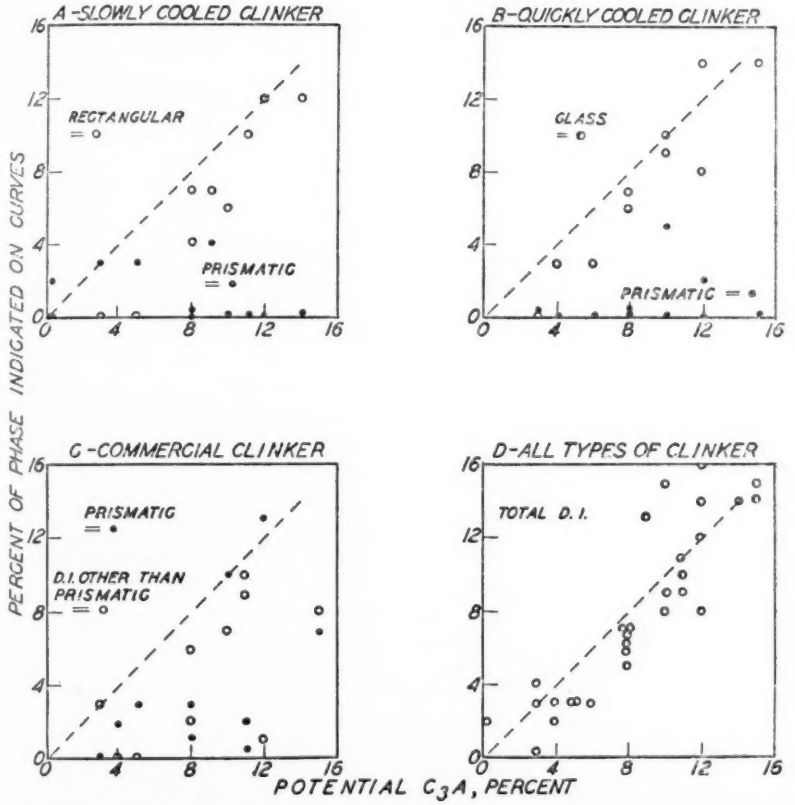

FIGURE 2.—*Relationship between the potential* $3CaO.Al_2O_3$ *and the three types of dark interstitial material in clinkers subjected to different rates of cooling.*

[From data by Ward]

that very rapid cooling may prevent crystallization of the prismatic phase.

3. In the slowly cooled clinkers, rectangular $3CaO.Al_2O_3$ apparently formed at the expense of the prismatic phase. The presence of as much as 1 percent of alkali did not interfere with this action.

These data suggest that the prismatic material is not a stable phase and that an intermediate rate of cooling may be a requisite for its formation. If the cooling rate is slow, that is, of a rate approaching that required for equilibrium conditions, the stable rectangular $3CaO.Al_2O_3$ is formed regardless of the alkali content of the clinker.

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2. IN THE SYSTEM $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$

In a study of the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ [6], the only crystalline phase other than the components observed to be present under equilibrium conditions was the compound $3CaO.Al_2O_3$, normal in crystalline form and optical properties. No evidence was obtained of any high-temperature forms of any of the compounds of the system.

If the prismatic dark interstitial material can be produced by means of rapid cooling in charges of mixtures having compositions

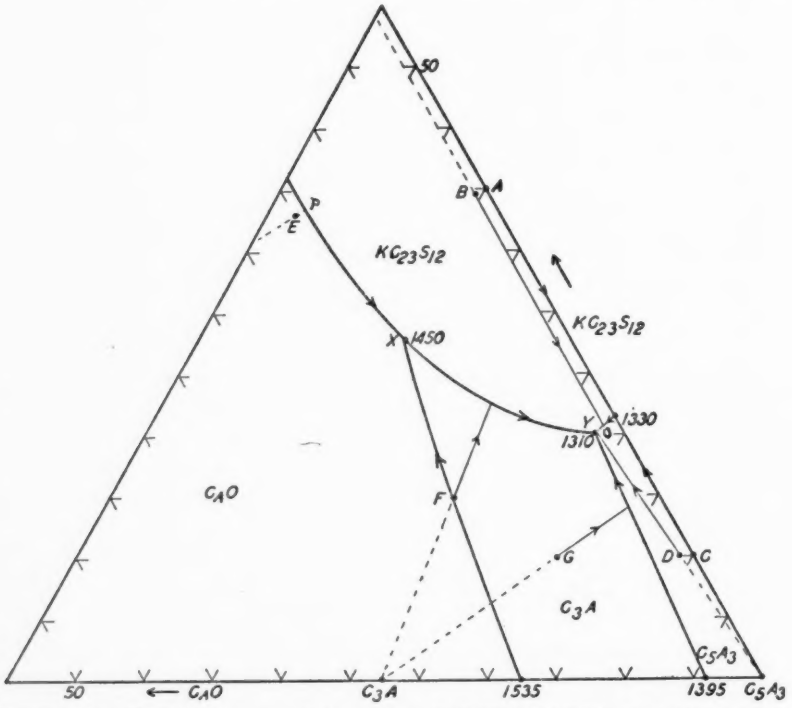


FIGURE 3.—*Partial diagram of the system* $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ *showing courses of crystallization when certain melts are cooled.*

$KC_{23}S_{12}=K_2O.23CaO.12SiO_2$.
$C_3A=3CaO.Al_2O_3$.
$C_5A_3=5CaO.3Al_2O_3$.

within this system, as it was in the case of the portland cement clinker, it may be concluded that this phase is a metastable phase that is formed as a result of rapid cooling and the formation of which is necessarily assisted by small amounts of alkali. Of course, it is conceivable that some systems may exist in which the prismatic phase is stable, but these systems do not appear to be related to portland cement clinker compositions.

Several mixtures previously employed in the study of the system $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$ were selected for the purpose of determining the relation of the prismatic phase to this system. A section of the phase-equilibrium diagram showing the boundary

curves separating the fields of stability is reproduced in figure 3. The compositions of the various charges being considered, and the crystallization curves followed under equilibrium conditions, are indicated on the diagram [6]. It is recognized that quickly cooled charges often do not follow the course of crystallization indicated by the equilibrium diagram, but in the cases about to be discussed, there was no evidence of serious departure from the curves.

(a) MIXTURES IN THE FIELD OF $K_2O.23CaO.12SiO_2$

Mixtures *A* and *B* in the field of $K_2O.23CaO.12SiO_2$ (see fig. 3) were prepared, having the following composition: Mix *A*, 40.0% of $K_2O.23CaO.12SiO_2$; 60.0% of $5CaO.3Al_2O_3$; and 0% of CaO. Mix *B*, 39.6% of $K_2O.23CaO.12SiO_2$; 59.4% of $5CaO.3Al_2O_3$; and 1.0% of CaO.

Charges of mixture *A* in the binary system $K_2O.23CaO.12SiO_2$-$5CaO.3Al_2O_3$ were heated to 1,490° C and then cooled to a quenching temperature of 1,260° C at rates varying from 30° C per minute to 4° C per minute. According to the diagram, no crystalline phases other than $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$ should exist, and these compounds are known to be unaffected by the usual water-etching treatment. Polished sections of these charges were prepared. In no case were any distinguishing features brought out by an attempted etching of the polished section in water for 2 seconds; that is, no phase of the charge was noticeably affected by this treatment. Examination of the powdered samples revealed that the charges cooled at rates more rapid than 10° C per minute were composed of crystals of the above compounds and glass but, when cooled at slower rates, only $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$ were present.

Mixture *B* falls within the compositional triangle formed by connecting the points representing the compositions $K_2O.23CaO.12SiO_2$, $3CaO.Al_2O_3$, and $5CaO.3Al_2O_3$. The completely crystallized product of a melt of any mixture falling within this triangle is composed of these three compounds only. When the melt of mixture *B* is cooled, crystals of $K_2O.23CaO.12SiO_2$ alone are formed until the temperature at the boundary between the fields of $K_2O.23CaO.12SiO_2$ and $5CaO.3Al_2O_3$ is reached (point *O*). On further cooling, these two compounds separate out together until the temperature falls to that of the eutectic, *Y*. At this point, $K_2O.23CaO.12SiO_2$, $5CaO.3Al_2O_3$ and $3CaO.Al_2O_3$ crystallize simultaneously.

Charges of this mixture were given the same thermal treatments as those given mixture *A*. Polished sections for the most part consisted of material that was not etched by a 2-second immersion in water. In this respect the sections appeared similar to those of mixture *A*, but they differed in that they contained readily etched material in localized clusters. Fields in which concentrations of the readily etched material occurred were photographed. Figure 4 (A) is a photomicrograph of a polished section of a charge of mixture *B* that was cooled slowly at a rate of 4° C per minute. The darkly etched crystals are typical of rectangular $3CaO.Al_2O_3$. No prismatic dark material was observed in any portion of the charge. When a charge of the same mixture was cooled more rapidly, at a rate of 15° C per minute, no rectangular $3CaO.Al_2O_3$ was evident but dark prismatic material was formed. A localized cluster of the prismatic crystals is shown in figure 4 (B). In this charge and in other charges containing no Fe_2O_3, the mean

index of the prismatic phase was about 1.70, with a birefringence of 0.008 to 0.010.

(b) MIXTURES IN THE FIELD OF $5CaO.3Al_2O_3$

Similar results were obtained in studies on mixtures *C* and *D* falling in the field of $5CaO.3Al_2O_3$ (fig. 3) having the following compositions: Mix *C*, 10.0% of $K_2O.23CaO.12SiO_2$; 90.0% of $5CaO.3Al_2O_3$; and 0% of CaO. Mix *D*, 10.0% of $K_2O.23CaO.12SiO_2$; 89.0% of $5CaO.3Al_2O_3$; and 1.0% of CaO. No material that was appreciably etched by water after 2 seconds was observed in any of the charges prepared from mixture *C*. On the other hand, small amounts of rectangular $3CaO.Al_2O_3$ were observed in the slowly cooled samples of mixture *D*, and small amounts of the prismatic dark material in the rapidly cooled charges of that composition.

These results indicate that a requisite for the formation of material which may be etched by water in accordance with the procedure herein used is the existence of potential $3CaO.Al_2O_3$ in the mixture. The addition of 1 percent of CaO to mixtures *A* and *C* increased the potential $3CaO.Al_2O_3$ from 0.0 to 3.6 percent, and resulted in the formation of dark prismatic crystals or rectangular $3CaO.Al_2O_3$, depending on the heat treatment.

(c) MIXTURE IN THE FIELD OF CaO

Mixture *E* (fig. 3), having the composition: 38.0% of $K_2O.23CaO.12SiO_2$; 47.0% of $5CaO.3Al_2O_3$; and 15.0% of CaO, is located in the CaO field, close to the boundary curve between the fields of CaO and $K_2O.23CaO.12SiO_2$. One charge of this mixture was melted at 1,615° C, cooled to the temperature of the quintuple point 1,450° at a rate of 2° C per minute, and then quenched. The phase diagram indicates that on cooling, CaO first separates from the melt, then when point *P* is reached, CaO and $K_2O.23CaO.12SiO_2$ crystallize together. No $3CaO.Al_2O_3$ crystallizes until the temperature falls below the quintuple point *X*, at 1,450° C. Examination of a polished section revealed the presence of rounded grains of CaO and of $K_2O.23CaO.12SiO_2$ embedded in a glass that was fairly readily etched by water. Neither the prismatic phase nor rectangular $3CaO.Al_2O_3$ was present. A second charge was cooled through the same range at the rapid rate of 30° C per minute. This specimen contained CaO, poorly crystallized grains of $K_2O.23CaO.12SiO_2$, and glass; but no prismatic material nor rectangular $3CaO.Al_2O_3$. Figure 5 (A) shows the appearance of the polished surface of the second charge after the water etch. The dark CaO grains, the light clusters of $K_2O.23CaO.12SiO_2$, and the glass may be noted.

A third charge of mixture *E* was cooled to a lower temperature, namely from 1,650° to 1,330° C, at an intermediate rate of 7° C per minute. Crystallization in this charge would tend to occur as follows: first CaO; then CaO and $K_2O.23CaO.12SiO_2$ to point *X*, at 1,450° C, where $3CaO.Al_2O_3$ first appears; below 1,450° C, CaO disappears entirely and $3CaO.Al_2O_3$ and $K_2O.23CaO.12SiO_2$ crystallize together along the boundary *XY*. No $5CaO.3Al_2O_3$ should appear because the eutectic temperature, 1,310° C, is not reached. Microscopical examination of a polished section showed it to contain rectangular $3CaO.Al_2O_3$, $K_2O.23CaO.12SiO_2$, and glass. No prismatic material was present. As shown in figure 5B, the $3CaO.Al_2O_3$ crystals were very

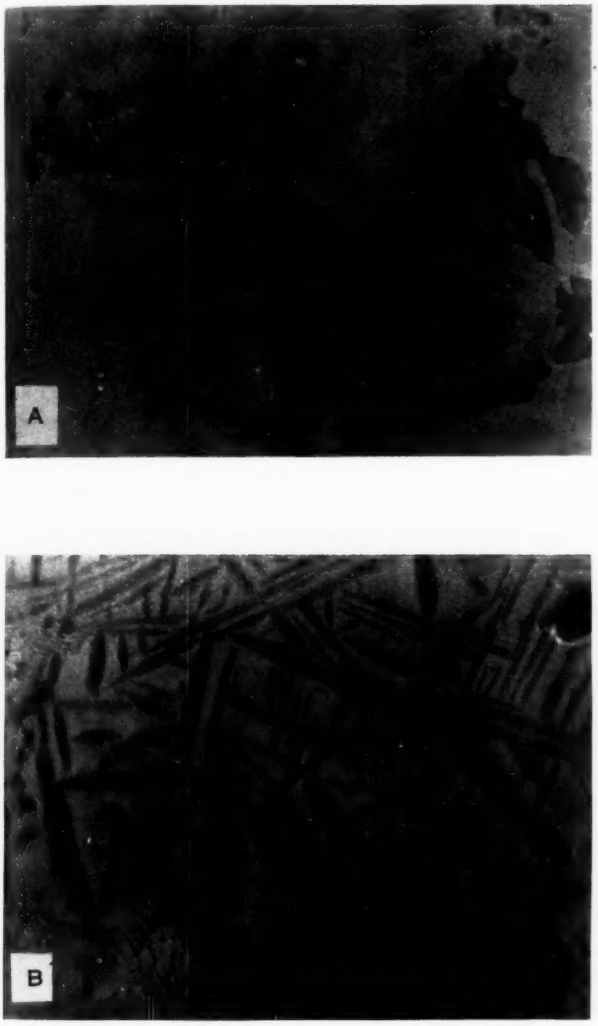


FIGURE 4.—*Polished sections of charges prepared from mixture B and quenched from a temperature below* $3CaO.Al_2O_3$ *liquidus; water-etched 2 sec.; reflected light,* $\times 500$.

A, Slowly cooled charge, shows rectangular $3CaO.Al_2O_3$; *B*, rapidly cooled charge, shows prismatic crystals.

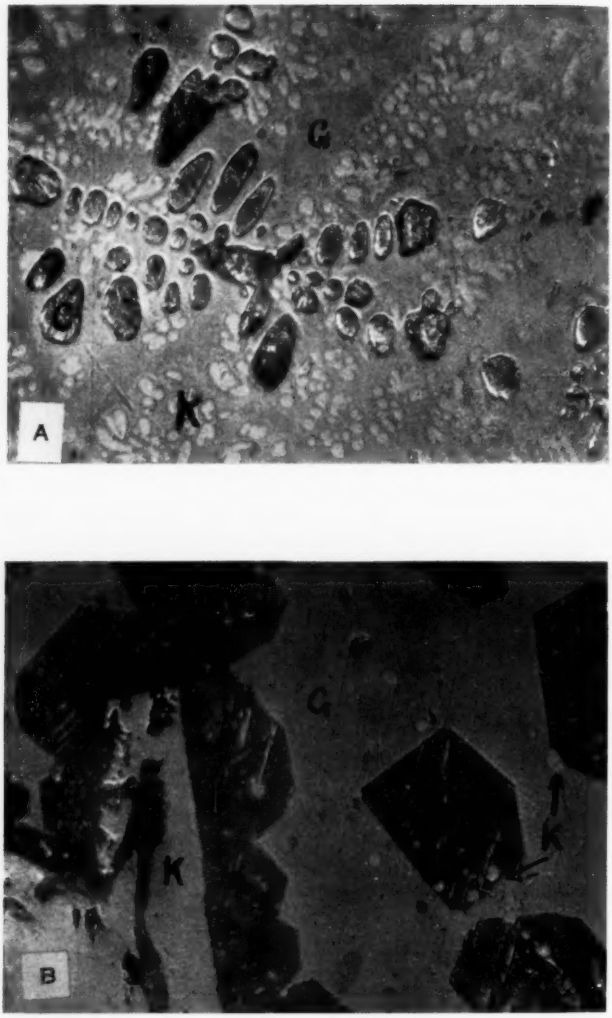


FIGURE 5.—*Polished sections of charges prepared from mixture E; water-etched 2 sec; reflected light,* $\times 500$.

A, Rapidly cooled charge quenched from temperature above $3CaO.Al_2O_3$ liquidus. Shows CaO (*C*), $K_2O.23CaO.12SiO_2$ (*K*), and glass (*G*); *B*, slowly cooled charge quenched from temperature below $3CaO.Al_2O_3$ liquidus. Shows large rectangular crystals of $3CaO.Al_2O_3$ (*R*), inclusion crystals of $K_2O.23CaO.12SiO_2$ (*K*), and glass (*G*).

FIGURE 5.—(*Continued*)

C, Rapidly cooled charge quenched from same temperature as *B*. Shows prismatic crystals (*P*), K_2O. $23CaO.12SiO_2$ (*K*), glass (*G*), and evidence of the formation of rectangular $3CaO.Al_2O_3$ (*R*).

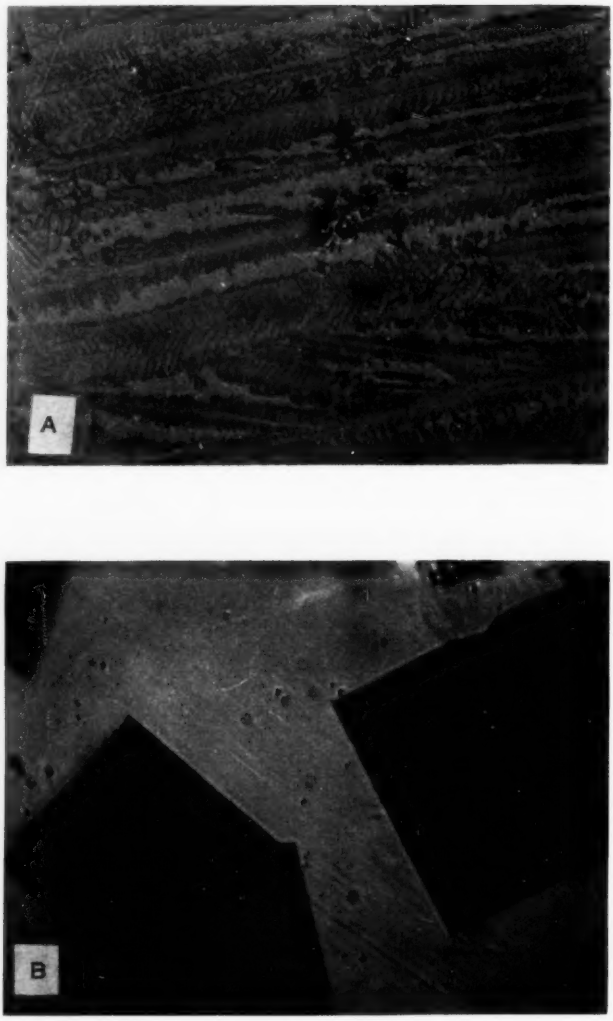


FIGURE 6.—*Polished sections prepared from mixture F; water-etched 2 sec; reflected light, ×500.*

A, Rapidly cooled charge quenched from temperature below $3CaO.Al_2O_3$ liquidus. Shows alignment of small rectangular $3CaO.Al_2O_3$ grains and long irregular prismatic crystals; *B*, slowly cooled charge quenched from same temperature as *A*. Shows large crystals of rectangular $3CaO.Al_2O_3$ in glass.

large, and the $K_2O.23CaO.12SiO_2$ crystals were present as inclusions in the $3CaO.Al_2O_3$ or had their shape determined to a large extent by the $3CaO.Al_2O_3$ grains.

A fourth sample was cooled through the same range as the previous sample but at the rapid rate of 30° C per minute. As shown in figure 5 (C), most of the darkly etched material was of the prismatic form. There was evidence that the formation of rectangular $3CaO.Al_2O_3$ was under way.

A fifth charge was cooled from 1,650° C at the rapid rate of 30° C per minute to a temperature of 1,440° C, which is just below the temperature at which $3CaO.Al_2O_3$ first appears (1,450° C). In the polished section of this charge, a relatively small amount of prismatic material, some residual CaO, poorly crystallized $K_2O.23CaO.12SiO_2$, and glass were observed. No rectangular $3CaO.Al_2O_3$ appeared to be present.

It is sometimes difficult or impossible to identify with certainty all of the material shown in a polished surface of a sample that has been etched only by water. In the specimens discussed above, all the phases mentioned, and only those, were observed in powdered samples of the respective charges. In this discussion, interest is centered chiefly on the water-etched material.

In the above study neither charge that was quenched at a temperature above that at which $3CaO.Al_2O_3$ first appears contained any of the prismatic phase nor any rectangular $3CaO.Al_2O_3$. When quenched below this temperature, the slowly cooled specimen contained rectangular $3CaO.Al_2O_3$, but no prismatic material, whereas the rapidly cooled samples contained the prismatic phase.

(d) MIXTURES IN THE FIELD OF $3CaO.Al_2O_3$

With melts of compositions from which, according to the phase diagram, $3CaO.Al_2O_3$ is the first solid phase to appear, it was found that there is a very narrow range in cooling conditions conducive to the formation of the prismatic material. Mixture *F* on the boundary separating the fields of CaO and of $3CaO.Al_2O_3$ and mixture *G* in the field of $3CaO.Al_2O_3$ were prepared (see fig. 3), having the following compositions: Mix *F*, 15.0% of $K_2O.23CaO.12SiO_2$; 70.0% of $5CaO.3Al_2O_3$; and 15.0% of CaO. Mix *G*, 10.0% of $K_2O.23CaO.12SiO_2$; 80.0% of $5CaO.3Al_2O_3$; and 10.0% of CaO.

Upon cooling melts of these mixtures as rapidly as 30° C per minute, the prismatic phase usually was surrounded with a sheath of isotropic material having the optical properties of $3CaO.Al_2O_3$. Often in the same charge, trains of small crystals of rectangular $3CaO.Al_2O_3$ were alined as though they had resulted from an original prismatic crystal. An example of this condition is shown in figure 6(A), which is a photomicrograph of a water-etched polished section of a charge of mixture *F*. This charge was cooled from 1,475° to 1,375° C at the rapid rate of 30° C per minute. The alinement of the small, rectangular $3CaO.Al_2O_3$ grains and the long, irregular, prismatic crystals are evident in the field shown in this photomicrograph. At rates of cooling more rapid than 30° per minute, bundles of fibrous crystals formed. Apparently these were the prismatic crystals in question, since they were etched by water, but they were too fine to permit an accurate determination of their optical properties. When the same composition was cooled through the same range very slowly, 4° C per minute, no prismatic material was present, but large

crystals of rectangular $3CaO.Al_2O_3$ in glass were formed, as shown in figure 6(B).

These and comparable studies dealing with compositions within the system $K_2O.23CaO.12SiO_2$–CaO–$5CaO.3Al_2O_3$ furnish evidence that the prismatic phase may be a metastable form of $3CaO.Al_2O_3$ that crystallizes when charges containing potash are cooled at rapid rates. The prismatic phase did not appear in charges of any composition falling outside of the regions of the system where $3CaO.Al_2O_3$ appears at complete crystalline equilibrium, nor did it ever appear in charges quenched from temperatures above those of the liquidus for $3CaO.Al_2O_3$ as defined in the phase-equilibrium diagram (fig. 3). On the other hand, the prismatic phase did appear in charges quenched from temperatures below those of the liquidus for $3CaO.Al_2O_3$.

3. IN MIXTURES OF COMPOSITIONS BEYOND THE LIMITS OF THE SYSTEM $K_2O.23CaO.12SiO_2$-CaO-$5CaO.3Al_2O_3$

In a previous investigation by the author [5], it was reported that a mixture (*H*), represented by $3(3CaO.SiO_2)+9(2CaO.SiO_2)+K_2O.Al_2O_3+Fe_2O_3$, was heated to 1,400° C and cooled to 1,295° C at the slow rate of 2.5° C per minute, and that the product consisted of only two phases; $K_2O.23CaO.12SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$. In the present study, this mixture was heated to 1,450° C and then cooled to 1,295° C at various rates more rapid than the above. These charges all crystallized readily and consisted of $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O$ and small amounts of glass, varying somewhat with the rate of cooling. In no case was any prismatic dark interstitial material observed.

Another preparation (*I*) was made, using 75 percent of mix $H+25$ percent of $3CaO.Al_2O_3$. One sample was heated to 1,400° C and cooled to 1,295° C at the slow rate of 2° C per minute. This charge contained only $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and rectangular $3CaO.Al_2O_3$. A second sample cooled through the same range at the more rapid rate of 10° C per minute contained $K_2O.23CaO.12SiO_2$, $4CaO.Al_2O_3.Fe_2O_3$, and the prismatic phase. No rectangular $3CaO.Al_2O_3$ and very little glass were observed. The prismatic dark interstitial material in this, and other charges containing Fe_2O_3, had indices of refraction that agreed with those reported by Insley and McMurdie [1] for this phase.

The above results indicate that the prismatic dark interstitial material cannot be formed unless some of the Al_2O_3 in a mixture is potentially available for $3CaO.Al_2O_3$ (Al_2O_3:Fe_2O_3>0.64). Again the results suggest that the components of $3CaO.Al_2O_3$ may crystallize in either of two forms—isotropic rectangular or anisotropic prismatic. The rate of cooling appears to be the determining factor.

It was desired to determine what effect an excess of K_2O over that required for the compound $K_2O.23CaO.12SiO_2$ might have on the formation of the prismatic and the rectangular phases. Assuming that this excess K_2O would form $K_2O.Al_2O_3$ [3], a mixture (*J*) was designed to contain the following phases after being heated and cooled under equilibrium conditions: 19.3% of $K_2O.23CaO.12SiO_2$; 19.6% of $K_2O.Al_2O_3$; 60.7% of $3CaO.Al_2O_3$; and 0.4% of CaO.

In a charge heated to 1,400° C and cooled to 1,320° C at the very slow rate of ½° C per minute, all of the above phases and a small

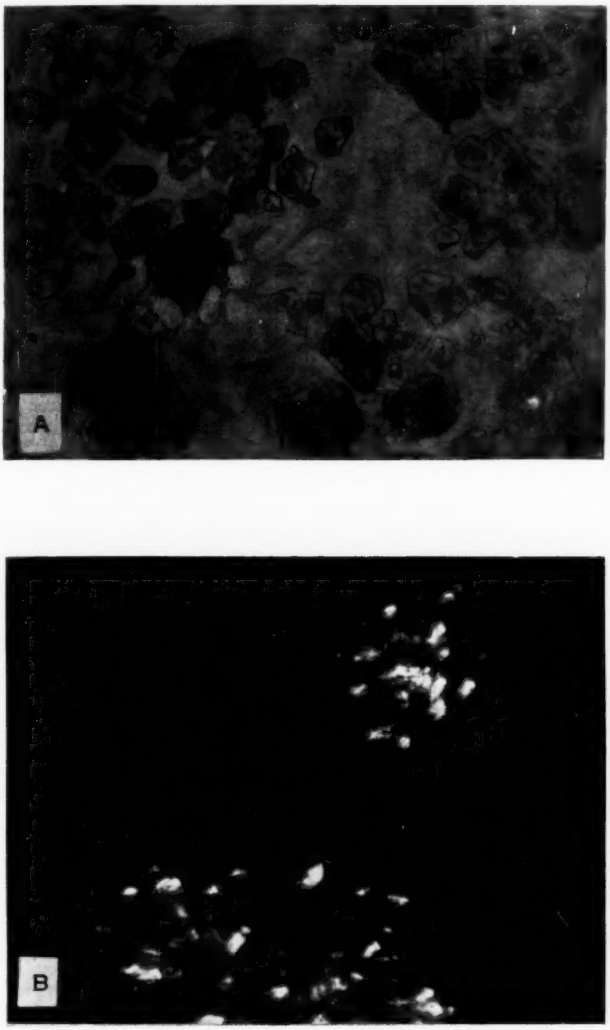
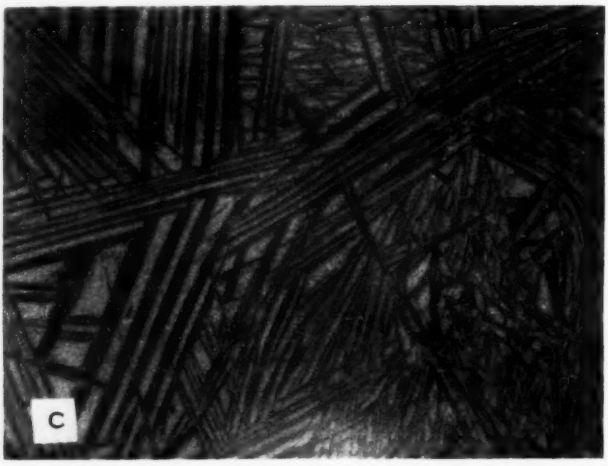


FIGURE 7.—*Polished thin sections prepared from mixture J.*

A, Polished surface of slowly cooled charge; water-etched 3 sec; reflected light; magnification, ×1000. Rectangular $3CaO.Al_2O_3$, $K_2O.23CaO.12SiO_2$, and glass present; *B*, same field as *A* but viewed with transmitted light, crossed nicols. Shows birefringent $K_2O.23CaO.12SiO_2$;



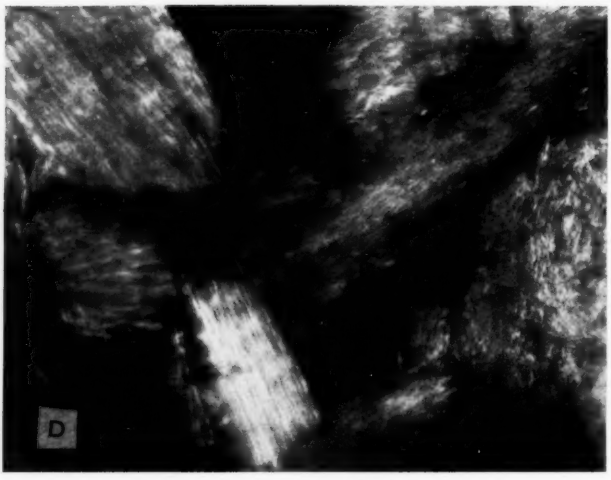


FIGURE 7.—(*Continued*).

C, Polished surface of rapidly cooled charge quenched from same temperature as *A*; water-etched 2 sec; reflected light; magnification ×1000. Shows abundant growth of dark prismatic crystals; *D*, same field as *C* but viewed with transmitted light, crossed nicols. Show birefringent prismatic crystals.

amount of glass were observed by examination of powdered samples in oil. The $3CaO.Al_2O_3$ was in the isotropic form.

Two charges of this mixture (*J*) were then differently heat treated and polished thin sections prepared. Both charges were heated to 1,500° C and then cooled to 1,370° C. The first charge was cooled slowly at a rate of 1½° C per minute. Figure 7 (A) shows the appearance of the water-etched polished surface in reflected light. The well-formed crystals of rectangular $3CaO.Al_2O_3$ and the absence of prismatic crystals may be noted. Figure 7 (B) shows the same field viewed by transmitted light through crossed nicols. The clusters of birefringent material are $K_2O.23CaO.12SiO_2$. The second charge was cooled more rapidly at a rate of 10° C per minute. Glass, a small amount of CaO, poorly crystallized grains of $K_2O.23CaO.12SiO_2$, and much prismatic dark material were observed. Figure 7 (C) is a photomicrograph of the surface after etching with water for 2 seconds. This figure may be compared with figure 7 (A), the only variable being the rate of cooling. Figure 7 (D) shows the same field (7, C) viewed by transmitted light through crossed nicols. The abundance of birefringent prismatic crystals may be noted.

It should be mentioned that efforts to obtain the prismatic modification in compositions containing no SiO_2 were unsuccessful. Although the study of the relation of the prismatic phase to the system $K_2O.23CaO.12SiO_2$–CaO–$5CaO.3Al_2O_3$ has indicated that the composition of this phase is very close to that of $3CaO.Al_2O_3$, the possibility remains that some SiO_2 (and possibly other components) is present in solid solution or is an integral part of the unit-cell structure. In either case the amount of SiO_2 involved must be small. No measurable reductions in the amount of the observed total calcium silicates, as compared with the theoretical amount calculated as being present, have been found by other workers to occur in clinkers containing appreciable amounts of the prismatic phase [8, 10]. Any crystalline $K_2O.23CaO.12SiO_2$ present likely was included with the amounts of the calcium silicates reported in the data to which reference has been made. The above potash compound was not known at the time of these studies. L. S. Brown has recently reported that he has observed $K_2O.23CaO.12SiO_2$ in sections of commercial clinker [14].

In the present study, the formation of the prismatic phase was induced by adding as little as 5 percent of $3CaO.SiO_2$ to a mixture containing 11.0 percent of K_2O, 48.0 percent of CaO, and 41.0 percent of Al_2O_3. The 1.32 percent of SiO_2 introduced by this amount of $3CaO.SiO_2$ would be sufficient to form 3.85 percent of $K_2O.23CaO.12SiO_2$. Small quantities of this latter compound were observed in the charges, but no exact measurements of the amounts were made because, in these particular cases, some of the components likely were contained in the glass that also was present.

4. EFFECT OF K_2O AS K_2SO_4 ON THE FORMATION OF THE PRISMATIC MATERIAL

It has been reported by the author, in connection with another investigation [6], that in mixtures of K_2O, CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2 and SO_3 comparable to portland cement clinker, K_2O combines preferentially with SO_3 to form K_2SO_4, and that any K_2O in excess of that required for K_2SO_4 combines with CaO and

SiO_2 to form $K_2O.23CaO.12SiO_2$. It was shown also in the same study that the components of K_2SO_4 do not enter the clinker melt, molten K_2SO_4 being immiscible with the liquid composed of other clinker components. Since K_2O in the form of K_2SO_4 is not contained in the melt from which the prismatic phase crystallizes, K_2O in this form would not be expected to aid in the formation of the prismatic material.

Mixture *K* was prepared adding 10 percent of K_2SO_4 to 90 percent of the mixture that corresponds to the liquid composition for an Al_2O_3:Fe_2O_3 ratio of 2.62 on the $3CaO.SiO_2$–$2CaO.SiO_2$ surface at 1,400° C in the quaternary system CaO–Al_2O_3–Fe_2O_3–SiO_2 [13]. The composition of the resulting mixture *K* was 50.7% of CaO; 23.6% of Al_2O_3; 9.0% of Fe_2O_3; 6.7% of SiO_2; and 10.0% of K_2SO_4. Charges of this preparation were cooled through various temperature ranges and at various rapid rates. Although the CaO–Al_2O_3–Fe_2O_3–SiO_2 portion of the sample had a potential $3CaO.Al_2O_3$ content of 17 percent, no prismatic dark interstitial material was observed in any of the charges.

Potassium oxalate was incorporated with mixture *K* in an amount calculated to give a mixture having 1 percent of K_2O in excess of that combined as K_2SO_4. A charge was cooled from 1,440° to 1,220° C at the rapid rate of 12° C per minute. A large amount of prismatic crystals was formed in this specimen.

Further studies were made in this connection with two other mixtures (*L* and *M*), in which all the K_2O was calculated to be present as K_2SO_4. These had the compositions: Mix *L*, 25.0% of $3CaO.SiO_2$; 25.0% of $2CaO.SiO_2$; 25.0% of $3CaO.Al_2O_3$; 0% of $4CaO.Al_2O_3.Fe_2O_3$; and 25.0% of K_2SO_4. Mix *M*, 35.0% of $3CaO.SiO_2$; 35.0% of $2CaO.SiO_2$; 15.0% of $3CaO.Al_2O_3$; 10.0% of $4CaO.Al_2O_3.Fe_2O_3$; and 5.0% of K_2SO_4. Charges of these two samples were cooled from 1,475° C at rates varying from 10° C per minute to the very rapid rate which obtained when the charge was removed from the furnace and allowed to cool in air. No prismatic dark interstitial material was observed in any of the specimens, confirming again the view that K_2O as K_2SO_4 does not aid in the formation of the prismatic phase.

IV. DISCUSSION

In the study of the system $K_2O.23CaO.12SiO_2$–CaO–$5CaO.3Al_2O_3$ [6], no evidence was obtained of the formation under conditions of equilibrium of prismatic dark interstitial material. This phase has been obtained in this and other systems only under conditions of nonequilibrium induced by rapid cooling. No range of real stability appears to exist for this phase. It would appear from the conditions, both thermal and compositional, necessary for the formation of the prismatic phase that it is a metastable form of $3CaO.Al_2O_3$, and monotropic (i. e., having no definite transition point) with respect to the stable, isotropic, rectangular $3CaO.Al_2O_3$.

It is not possible, on the basis of present data at least, to state definitely that the prismatic material has the composition exactly that of $3CaO.Al_2O_3$. The difficulties encountered in trying to determine the composition of a metastable phase, that thus far has been observed only in systems containing at least four oxide components, are evident. This phase has never been obtained in a pure state on which a chemical analysis or a melting-point determination could be made.

The ratio of the amount of prismatic material to the amount of alkali in various specimens has been found to be extremely variable. The maximum possible value of this ratio has not been established. It has been shown with certain compositions in this study that the amount of prismatic material formed appears to be limited by the calculated potential amount of $3CaO.Al_2O_3$. In certain other specimens, however, having high potential $3CaO.Al_2O_3$ contents, there was evidence that the optimum condition for the formation of the maximum amount of the prismatic phase did not prevail. This optimum condition often is not easily attained; too rapid cooling inhibits the crystallization of the potential quantity of the prismatic phase, and too slow cooling permits the formation of the rectangular form of dark interstitial material at the expense of the prismatic. With some compositions the range of cooling rates favorable to the formation of the prismatic material is extremely limited. It has been observed, with many samples in this study, that the prismatic phase would be concentrated near the surface, next to the platinum capsule enclosing it, and the rectangular form in the interior where the cooling was slightly slower. It has been observed also that some charges contained the prismatic phase in the interior and only the amorphous form of dark interstitial material (glass) near the surface.

It appears that the rate of cooling for the optimum formation of the prismatic phase varies with the composition of the raw mixture. For example, it was found that extremely rapid cooling was required for the production of the prismatic phase in charges having compositions within the field of $3CaO.Al_2O_3$ in the system $K_2O.23CaO.12SiO_2$-CaO–$5CaO.3Al_2O_3$. On the other hand, it was shown in the data obtained by Ward on heat-treated commercial clinkers that relatively slow cooling was favorable to the formation of the prismatic material in mixtures having low-potential $3CaO.Al_2O_3$ contents (low Al_2O_3: Fe_2O_3 ratios).

Indefinite results are obtained in attempts to establish the composition of the prismatic dark interstitial material by the measurement of the amounts of the phases in specimens of known oxide compositions for the following reasons:

1. Unless the amount of the prismatic phase closely approaches that of the calculated potential $3CaO.Al_2O_3$ in a sample, it is uncertain that a close approach has been made to the optimum conditions required for the formation of the prismatic material.
2. No etchant has yet been found to distinguish definitely the potash compound $K_2O.23CaO.12SiO_2$ from the two calcium silicates in polished sections of clinker. For this reason, it is difficult to identify and measure $K_2O.23CaO.12SiO_2$ with exactness. The amount of potash combined in this compound in a given sample, therefore, is difficult to determine.
3. Glass of an undeterminable composition (undeterminable because of the existence of nonequilibrium conditions) is commonly associated with the prismatic phase. It is probable that some alkali is contained in the glass.
4. Calculations of composition based on the quantities of the phases present may be considerably in error, because the extent to which solid solution may occur among the various phases is not known.

Certain comparisons that have been made between the observed amount of prismatic material and the chemically determined amount of

alkali in a specimen show that the amount of alkali which possibly could be a component of the prismatic phase is a very small percentage of the composition. For example, an experiment was made by heating a mixture composed of 10% of $K_2O.23CaO.12SiO_2$; 15% of $3CaO.Al_2O_3$; 20% of $4CaO.Al_2O_3.Fe_2O_3$; 30% of $3CaO.SiO_2$; and 25% of $2CaO.SiO_2$ to 1,530° C and then cooling to 1,290° C at a rate of 8° C per minute. An examination of a water-etched polished section [2] showed 14 percent of prismatic dark interstitial material and 2 percent of glass. If the K_2O in the $K_2O.23CaO.12SiO_2$ that may be present and the K_2O in the 2 percent of glass are not considered (for the reasons outlined above), it might be argued that the 0.5 percent of K_2O in the sample [3] is contained in the 14 percent of the prismatic material and, therefore, the K_2O content of this phase is 3.6 percent. (It will be recalled, however, that the maximum possible alkali content of the prismatic phase in clinker 20 of the group examined by Insley was calculated, on the above basis, to be only 1.4 percent.)

Just how K_2O (or Na_2O)[4] functions in the formation of the prismatic phase is not wholly clear. It is known that small amounts of certain compounds sometimes modify the crystalline form of another compound. Rankin and Merwin, in a study of the system CaO–MgO–Al_2O_3 [15] observed that a new form of alumina, β–Al_2O_3, occurred occasionally in charges of alumina that had been melted and slowly cooled. The presence of a small amount of MgO (0.5 percent) materially assisted in the formation of the new form, whereas melted alumina containing small amounts of either CaO or SiO_2 was found to crystallize on cooling as the α-form (corundum). Stillwell [16], in analyzing samples of β–Al_2O_3, came to the conclusion that the presence of Na_2O was essential for the formation of this form; in some samples, for example, the Na_2O content reached about 5 percent. On the other hand, in connection with the work of Rankin and Merwin, H. S. Washington analyzed a sample of β–Al_2O_3 that had been separated from artificial alumina abrasive and found it to be pure Al_2O_3. Later, Bragg, Gottfried, and West, in their study of the structure of β–Al_2O_3 [17], proposed a structure that contains Na+23Al+35 O atoms in the unit cell. This corresponds to the composition $Na_2O.23Al_2O_3$. In a still later study, Brownmiller observed that β–Al_2O_3 crystallizes in the binary system K_2O–Al_2O_3 [3]. Microscopical examinations of heated mixtures in this system showed the presence of two phases, $K_2O.Al_2O_3$ and β–Al_2O_3.

In the sense that β-alumina is referred to as a form of alumina because the material is essentially alumina, if not entirely so, it is suggested that the prismatic dark interstitial material be considered as prismatic $3CaO.Al_2O_3$. All the data thus far obtained indicate that the composition of the prismatic phase is at least very close to that of $3CaO.Al_2O_3$. No measurable reductions in the amounts of the calcium silicates have been observed upon the formation of this phase. This and the close relation between the amounts of prismatic material and the calculated potential amount of $3CaO.Al_2O_3$. in clinker indicate that if any components other than those of $3CaO.Al_2O_3$ are contained in the prismatic material, or if any solid

[2] By G. W. Ward.

[3] Analyzed by Leonard Bean. The 10 percent of $K_2O.23CaO.12SiO_2$ used in the original mixture contributes 0.46 percent of K_2O to the composition.

[4] Insley and McMurdie [1] have shown that the presence of Na_2O also promotes the formation of a prismatic phase having similar optical properties.

solution exists, the amount is so slight that consideration of the phase as $3CaO.Al_2O_3$ introduces no significant error in the computation of the compound composition of clinker. Furthermore, no evidence has been obtained, so far as is known, of the properties of cements being affected by the existence of one form to the exclusion of the other, and there appears to be no reason for modifying the clause in the specifications for certain cements which limits the calculated amount of $3CaO.Al_2O_3$ permitted.

The conditions apparently necessary for the formation of prismatic $3CaO.Al_2O_3$ are

(a) The composition of the raw mixture must be such as to permit potentially the formation of $3CaO.Al_2O_3$.

(b) The phase must crystallize from a melt that contains some K_2O, or Na_2O, or both, and SiO_2, although the amount of prismatic $3CaO.Al_2O_3$ formed appears to be independent of the amounts of these oxides.

(c) The rate of cooling must be such as to permit crystallization of the prismatic phase from the melt, but yet not subject these crystals to prolonged heat treatment. Slow cooling, which permits an approach to equilibrium conditions, favors the formation of isotropic, rectangular $3CaO.Al_2O_3$ at the expense of the anisotropic, prismatic $3CaO.Al_2O_3$.

V. SUMMARY

A study has been made of the nature of the prismatic dark interstitial material, so called because of its appearance in etched, polished sections of portland cement clinker.

Microscopical data obtained on commercial clinker by other investigators have been presented, and the relation of the amounts of the prismatic phase to the calculated potential amounts of $3CaO.Al_2O_3$ has been shown.

A study was made of the relation of the prismatic dark interstitial material to the system $K_2O.23CaO.12SiO_2$—CaO—$5CaO.3Al_2O_3$. It was found that in this system, the prismatic phase is not stable and does not appear in samples that have been cooled at rates approaching those of equilibrium conditions. It was obtained only under conditions of rapid cooling. Both thermal and compositional conditions found to be required for its formation suggest that it may be a metastable form of $3CaO.Al_2O_3$ and monotropic with respect to the stable, isotropic, rectangular $3CaO.Al_2O_3$.

The results of studies on samples having compositions beyond the limits of the system $K_2O.23CaO.12SiO_2$—CaO—$5CaO.3Al_2O_3$ likewise show the close relationship between $3CaO.Al_2O_3$ and the prismatic phase.

It was found that the K_2O which is combined as K_2SO_4 in clinker does not induce the formation of prismatic dark interstitial material.

While definite proof has not been presented that the composition of the prismatic phase is exactly that of $3CaO.Al_2O_3$, the data show the composition of the prismatic phase to be very close to that of $3CaO.Al_2O_3$. Since the amounts of the other clinker phases, and the properties of cements, do not appear to be affected measurably by the presence of one form of crystalline dark interstitial material to the exclusion of the other, it is suggested that the prismatic phase be considered as a metastable form of $3CaO.Al_2O_3$ and referred to as

"prismatic $3CaO.Al_2O_3$" instead of the indefinite term "prismatic dark interstitial material."

Conditions necessary for the formation of prismatic $3CaO.Al_2O_3$ have been outlined.

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